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# Study to Determine an Improved Method for Apollo Propellant System Decontamination and Propellant Tank Drying

Manned Spacecraft Center  
National Aeronautics and Space Administration  
Houston, Texas

Phase I-Interim Report

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**THE DOW CHEMICAL COMPANY**

**GOVERNMENT AFFAIRS**  
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April 28, 1966

National Aeronautics and Space Administration  
Manned Spacecraft Center  
Procurement and Contracts Division  
2101 Webster-Seabrook Road  
Houston, Texas

Attention: Mr. W. H. Brandenburg

Gentlemen:

The Dow Chemical Company hereby submits 9 copies of the Phase I Interim Report on Contract NAS 9-4605, "A Study to Determine an Improved Method for Apollo Propellant System Decontamination."

Sincerely,

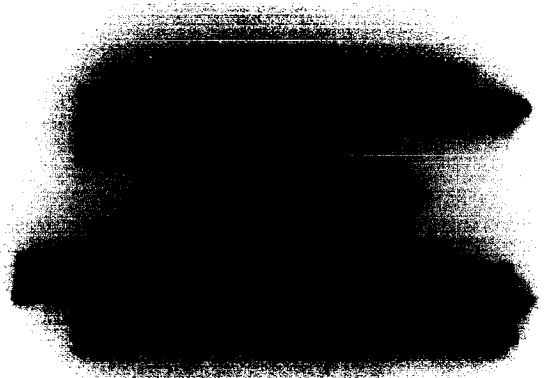
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# Study to Determine an Improved Method for Apollo Propellant System Decontamination and Propellant Tank Drying

Manned Spacecraft Center  
National Aeronautics and Space Administration  
Houston, Texas

Phase I-Interim Report

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The Dow Chemical Company  
Midland, Michigan

## I. ABSTRACT

This is an interim report describing the work accomplished in Phase I and submitted in partial fulfillment of NAS 9-4605 Contract, "A Study to Determine an Improved Method for Apollo Propulsion System Decontamination."

The work in this phase included studies of (1) compatibility of solvent with propellant and components, (2) methods of decontamination, (3) efficiencies of solvents, (4) temperature effect, (5) diffusion rate of propellant from elastomers, (6) removal of propellant from flushing solvents and (7) a survey of the published literature, proprietary information, and private correspondence on the technology of decontamination of rocket propulsion systems.

All experimental work in Phase I was done in laboratory bench-scale apparatus.

### III. APPROACH

Our approach involves three main areas of development effort -- the study of methods utilizing solvents known to be compatible with the contaminants, an evaluation of potentially unique solvents, and a study of unique methods of decontamination.

The development of methods includes a comparison of the decontaminating efficiencies of various solvents of known compatibility as well as optimization of the process by a study of such physical variables as time sequence, temperature, solvent mixtures, and batch versus continuous flow. An evaluation of methods of continuous solvent regeneration is also included.

Solvent development work consists of the selection, evaluation, and screening of candidate solvents for suitability by detonation testing and measurement of compatibility with system materials.

Methods research work is aimed at devising unique approaches to the problem. This includes a comparison of gaseous and vapor-phase procedures with the more conventional liquid solvent methods.

These development efforts are supported by functional units supplying the required analytical development, design engineering, and process evaluation.

A review of present technology and methods through literature and technical documents is of major importance to this study program.

The interrelation of these efforts is shown diagrammatically in Figure II-1.

#### IV. SIGNIFICANT RESULTS

- A. The results of the detonation tests show fourteen solvents or solvent mixtures were compatible with  $N_2O_4$ . No explosions occurred when the solvents were added to  $N_2O_4$  and the mixture shocked with a blasting cap. The compatible solvents are listed below:
1. Bromodichloromethane
  2. Tribromofluoromethane
  3. Freon<sup>®</sup> MF
  4. Freon<sup>®</sup> TF
  5. Freon<sup>®</sup> E-2
  6. Freon<sup>®</sup> 112
  7. Freon<sup>®</sup> C-318
  8. 1,1-Dibromo-2,2,2-trifluoroethane
  9. Dibromodifluoromethane
  10. Freon<sup>®</sup> 112 and Bromochloromethane mixture (1:1)
  11. Carbon tetrachloride
  12. Chloroform
  13. 2,2-Dichloro-1,1,1-trifluoroethane
  14. Perfluorodimethylcyclobutane
- B. The detonation tests with Aerozine-50 and the candidate solvents were inconclusive since there was no discernable difference in the order of magnitude of the explosion with or without the solvent.
- C. Correlating the results of some thermodynamic calculations with the knowledge of compatibility gained from the detonation tests, the following generalizations appear valid.
1. Solvent- $N_2O_4$  systems having a free energy change,  $\Delta F$  value less than 2 Kcal/gram  $N_2O_4$  do not detonate regardless of the size of the triggering charge. These solvents are compatible with  $N_2O_4$ .
  2. Solvent- $N_2O_4$  systems showing a  $\Delta F$  value greater than 2 Kcal/gram  $N_2O_4$  can be detonated given sufficient shock. These solvents are not compatible with  $N_2O_4$ .

- D. The results of the compatibility study of elastomers with candidate solvents are given below.
1. Teflon<sup>®</sup> TFE and FEP are compatible with the propellant and all solvents.
  2. Kel-F No. 300 was not compatible with the propellant. Failure occurred within one week in the N<sub>2</sub>O<sub>4</sub> test and within three weeks in the Aerozine-50 test.
  3. Kynar was found to be compatible with propellant and solvents.
  4. Stillman SR634-70 rubber was not compatible with Aerozine-50. Failure occurred within five weeks. By comparison, B. F. Goodrich IIR-50 butyl rubber showed a gain in tensile strength.
  5. Rulon was found to be compatible with propellant and solvents.
  6. Freon<sup>®</sup> E-2, a perfluoroether compound, was compatible with the fuel and oxidant and the elastomers in both systems.
- E. Decontamination by fill-empty flushing was compared with continuous flushing. The results show that:
1. The fill-empty flushing is more efficient for a given volume of solvent.
  2. The time required to reach the same contaminant concentration level is about equal for both flushing methods.
- F. No evidence was obtained that indicates either the fuel or oxidant was chemically adsorbed on the surface of the metal.
- G. The elastomers absorb substantial quantities of the propellants. Experimental results show that the amount of contaminant diffused from the elastomer per unit of time is proportional to the amount present at that time; therefore, the rate the contaminant diffuses from the elastomer can be expressed mathematically by this equation:

$$K = \frac{2.303}{t_2 - t_1} \cdot \log \frac{c_1}{c_2}$$

where:  $c_1$  = the initial concentration of contaminant  
 $c_2$  = the final concentration  
 $t_1$  = the initial time  
 $t_2$  = the final time

The constant (K) is the specific rate constant or velocity constant for a first order reaction.

1. The specific rate constant (K) for the diffusion of  $N_2O_4$  from Teflon<sup>®</sup> FEP at ambient temperature shows values of  $1.4 \times 10^{-3}$ ,  $1.5 \times 10^{-3}$ , and  $1.8 \times 10^{-3}$  in environments of  $GN_2$ , Freon<sup>®</sup> TF, and  $CCl_4$ . These nearly identical values show the diffusion rate to be essentially independent of environment.
  2. The diffusion of A-50 from Stillman rubber at ambient conditions in environments of  $GN_2$  and methanol shows a (K) value of  $3.06 \times 10^{-4}$  for both environments.
  3. The results of  $N_2O_4$  diffusion from Teflon<sup>®</sup> FEP tests made at  $25^\circ$ ,  $65^\circ$ , and  $100^\circ$  C using  $GN_2$  purge show (K) values of  $1.4 \times 10^{-3}$ ,  $3.4 \times 10^{-3}$ , and  $1.1 \times 10^{-2}$ . This implies that the diffusion rate is temperature dependent. Plotting these points on semilog paper shows a reasonable fit; therefore, the diffusion rate increases exponentially as the temperature is increased.
- H. The results of tests indicate that the flushing solvents can tolerate several hundred parts per million of the contaminant and still effectively extract the contaminant from the elastomer.
- I. Aerozine-50 is efficiently removed from methanol and Freon<sup>®</sup> 113 by cation exchange resin (Dowex<sup>®</sup> 50W-X8, 50-100 mesh,  $H^+$ ).
- J. Silica gel, water-swollen and containing dissolved sodium hydroxide, is a satisfactory method for removing  $N_2O_4$  from the flushing solvent.

V. RECOMMENDATIONS

- A. Vapor-phase flushing is the recommended procedure for decontamination since it has several advantages over liquid-phase flushing. The advantages are:
1. The latent heat of vaporization as well as the sensible heat of the solvent will be available to supply heat to the system.
  2. The solvent vapors should give better penetration into all areas than liquid-fill procedures.
  3. The condensation of the vapors on the surfaces continuously bathes these surfaces with clean solvent which removes the contaminant and solid particles.
  4. The amount of solvent required for vapor-phase flushing compared to liquid-phase flushing is reduced by a factor of 100 to 1000, depending upon the particular flushing solvent used.
- B. The solvents shown below are recommended for evaluation in Phase II. The higher boiling solvents are preferred.

<u>Oxidant</u>	<u>Fuel</u>
1. Freon <sup>®</sup> MF	1. Methanol
2. Freon <sup>®</sup> TF	2. Ethanol
3. Carbon tetrachloride	3. N-Propanol
4. Bromodichloromethane	4. Isopropanol
5. Freon <sup>®</sup> E-2	5. Freon <sup>®</sup> E-2

Freon<sup>®</sup> E-2 was the only solvent found that was compatible with both propellant components and elastomers in both systems.

- C. Extraction of the  $N_2O_4$  with sodium hydroxide-treated silica gel is the recommended method for removing  $N_2O_4$  from the flushing solvent.
- D. The recommended procedure for removing Aerozine-50 from the flushing fluid with cation exchange resin (Dowex<sup>®</sup> 50W-X8, 50-100 Mesh  $H^+$ ).



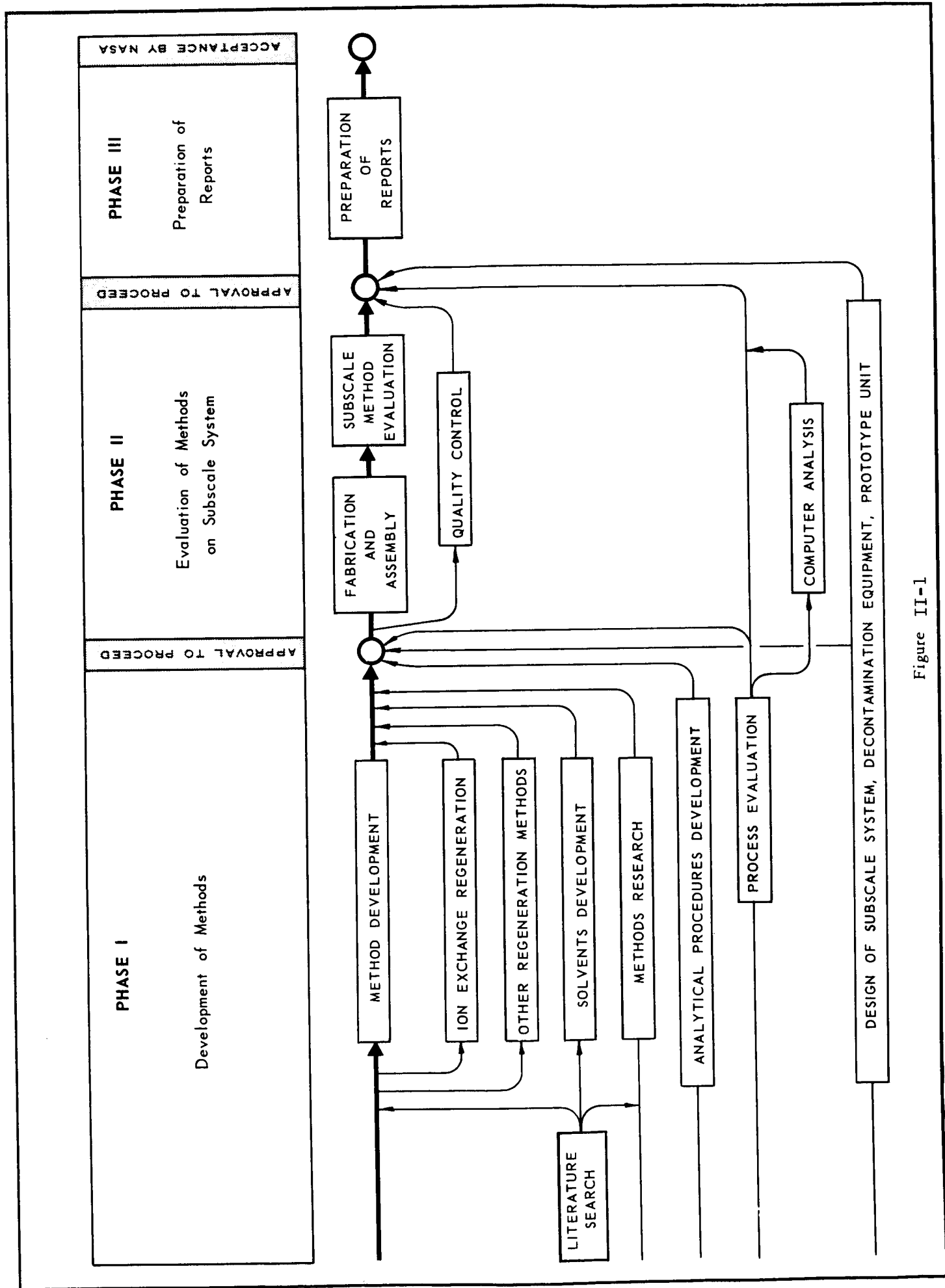


Figure II-1

## VI. UNIT 1 - METHODS DEVELOPMENT

### A. Summary

From the data obtained in this study the following conclusions can be made:

#### 1. Comparison between a fill and empty procedure and a continuous flow or recycle method

If the total volume of solvent required to reach a given contamination level is considered, the fill and empty procedure is the more efficient. If the total time required to reach a given contamination level is considered, the efficiencies of the two procedures are about equal, on the systems used in this phase of the project. Since the relative efficiencies are dependent upon the geometry of this system, this should be determined for the Apollo propulsion systems.

#### 2. Choice of solvents for N<sub>2</sub>O<sub>4</sub> decontamination

Solvents that passed the N<sub>2</sub>O<sub>4</sub> explosion test are included in Table 1-I. All solvents tested showed essentially the same efficiencies in removing N<sub>2</sub>O<sub>4</sub> from metal surfaces and from Teflon<sup>®</sup> soft parts. Mixtures of solvents showed no significant advantages.

Removal of N<sub>2</sub>O<sub>4</sub> from soft parts is a major problem area.

Increased soak times increased the removal of N<sub>2</sub>O<sub>4</sub> from Teflon<sup>®</sup>.

Elevated temperature increased the efficiency of the solvents in removing N<sub>2</sub>O<sub>4</sub> from Teflon<sup>®</sup> soft parts.

#### 3. Choice of solvents for fuel decontamination

Detonation tests indicate that if the fuel or a fuel-solvent mixture is detonated by a charge in the vapor, there is no explosion. If the fuel or fuel-solvent mixtures are subjected to detonation by a charge in the liquid phase, a low order explosion results. See Table 1-II for a list of solvent detonation tests.

Alcohols show better results than hydrocarbons or halogenated hydrocarbons in removing the fuel mixture from the test cylinders.

Removal of the fuel from the soft parts is difficult to obtain. Elevated temperatures increases the efficiency of the solvent in removing the fuel from the soft parts.

The work in this unit was involved in screening candidate solvents based upon tests for compatibility with the propellant (specifically solvent-propellant detonation tests), also, developing and evaluating methods utilizing solvents of known compatibility with the propellant and the materials of construction.

#### B. Detonation Test Procedure

The indiscriminate mixing of solvents with the propellants, especially  $N_2O_4$ , is likely to result in an explosive mixture. As a first precaution in the screening of solvents, a testing program was initiated which involved mixing various solvents with  $N_2O_4$  on Aerozine-50 and shocking or igniting the mixture with a blasting cap to determine if the mixture is explosive. These tests were carried out in an isolated area.

The procedure and equipment used were as follows:

- Ignition Source - E-83 electric blasting cap
- Sample Holder - 32-ounce paper Dixie cup
- Volume of nitrogen tetroxide - same volume as test solvent
- Volume of test solvent - as shown in Table 1-I

A paper Dixie cup containing the indicated volume of test solvent was placed on the sand. An equal volume of nitrogen tetroxide was poured remotely into the test solvent. An E-83 electric blasting cap was then detonated, by means of a six-volt battery, in the liquid mixture. The procedure used for the A-50 detonation tests was essentially the same as given above except the initial tests were carried out in vapor phase, and 100 ml of A-50 and solvent were used in all tests. Test results show that placing the blasting cap in the liquid gave a more sensitive and reproducible test. Therefore, the latter A-50 detonation tests and all of the  $N_2O_4$  tests were carried out with the blasting cap in the liquid. The detonation tests were empirical and the explosibility was estimated by concussion, audible, and visual observations. Usually, a crater of some dimension was made in the sand after the tests in which an explosion occurred. The size of the crater was proportional to the charge and intensity of the explosion.

#### C. Propellant-Solvent Detonation Tests

The results of the solvent- $N_2O_4$  detonation tests are given in Table 1-I. The tests were carried out in triplicate and shown only once unless there was a discrepancy in the results. Dibromochloromethane gave inconsistent results, and analysis of the sample by vapor phase chromatography revealed nothing that would account for this discrepancy. Trichloroethylene, which was known to be not compatible with  $N_2O_4$ , was included

in the tests to serve as a control since a high order explosion occurred when detonated with  $N_2O_4$ . A few low-boiling solvents such as Freon<sup>®</sup> C-318,  $(CF_2)_4$ , and dibromodifluoromethane were included, but it was necessary to pack the cup in dry ice to prevent evaporation.

The results of the A-50-solvent detonation tests are shown in Table 1-II. The initial tests were carried out in the vapors above the solution. This resulted in burning the materials, and no explosion occurred. Placing the detonator (blasting cap) in the A-50 solution, with no solvent present, resulted in a low order explosion. When a solvent was added and the test was carried out in the same manner, a low order explosion again occurred. There was no discernible difference in the order of magnitude of the explosion with or without the solvent; therefore, the A-50 detonation tests were discontinued.

#### D. Evaluation of Methods for $N_2O_4$ Decontamination

The apparatus shown in Figures 1-1, 1-2, 1-3, and 1-4 was used to evaluate the  $N_2O_4$  decontamination methods. Figure 1-1 shows the first system, and it was used to evaluate a continuous flushing method. The tests were carried out in the following manner: The test vessel was contaminated with approximately one milliliter of  $N_2O_4$ . A measured volume of solvent from the reservoir was then introduced into the vessel. The solvent was allowed to remain in the test chamber for a given period of time. Then the solvent in the test chamber was displaced with clean solvent from the reservoir. This procedure was repeated several times, and the  $N_2O_4$  concentration in each cycle was determined. The results were erratic, probably due to poor mixing. The final flush was withdrawn from the bottom, and it consistently contained more  $N_2O_4$  than did the displaced solvent.

The system was revised, and the modified apparatus is shown in Figure 1-2. The revised system permitted the fill-empty method as well as the continuous flushing method to be evaluated. The procedures used to evaluate the continuous flushing method was the same as described above. The overflow drainpipe was lowered to allow the solvent to drain from the test chamber in the fill-empty method.

The apparatus shown in Figure 1-3 is a refinement of the two previous systems. As shown in the above figure, a second test vessel was added to the system which made it possible to study the decontamination of elastomers that had been preexposed to contaminants. Also, provisions were made for sampling the exit gas.

A number of runs were made, using three different solvents, to establish a comparison between a fill and empty procedure and a continuous flow or recycle method. The equipment illustrated in Figure 1-2 was utilized in this work. The contaminant used was nitrogen tetroxide. The results obtained for each of the three solvents were essentially the same. The data obtained clearly indicate that, if we consider the total volume of solvent required to reach a given contamination level, the fill and empty procedure is the more efficient. This is illustrated by three solvents in Figure 1-5. The linear relationship between the volume of solvent and the log of the effluent concentration in the continuous flow method should be noted. In a situation where the solvent can be repurified and reused on site, the efficiency as measured by total volume passed through the system might not be of prime significance. Therefore, calculations were made to gain some insight into the comparative efficiencies of the two procedures in regard to total elapsed time. It was assumed that a reasonable flow rate into and through the propulsion system is 70 gpm and that a fill-soak-empty cycle for the batch procedure would require ninety minutes. Under these conditions, the efficiencies of the two procedures are about equal. Since this study proposes a system utilizing regeneration and recycle of the solvent, the elapsed time will probably be of more significance than the amount of solvent passed through the system. Remaining bench-scale work in Phase I was confined to the fill and empty method since it is less dependent upon the over-all geometry of the system.

#### E. Evaluation of Solvents for N<sub>2</sub>O<sub>4</sub> Decontamination

Efforts were made to distinguish between the cleaning efficiencies of various solvents. The apparatus shown in Figure 1-2 (without the Ti-Al filings) was used to carry out the tests. The fill-empty method using three flushes reduced the N<sub>2</sub>O<sub>4</sub> concentration in the third flush below five parts per million for all solvents. The solvents used were carbon tetrachloride, chloroform, and Freon® TF. The results are shown by the curves in Figure 1-5. The slopes of the curves in this figure indicate no apparent difference in the cleaning efficiency of the solvents. To complicate the system, the test chamber was filled about two-thirds full of Ti-Al filings along with some stainless steel wire cloth as illustrated in Figure 1-2. The results are shown by the curves in Figure 1-6. Again, no apparent difference was detected.

A two-chamber system, Figure 1-3, was constructed with one chamber available for the addition of soft parts. The soft parts consist of 14 inches of Teflon® TFE tubing with a surface area of 106 square centimeters. This tubing was soaked overnight in N<sub>2</sub>O<sub>4</sub> and then placed in one of the chambers. One

milliliter of liquid  $N_2O_4$  was added to the other chamber. Inspection of the curves in Figure 1-7 shows that it requires much more solvent, consequently a longer time to remove the  $N_2O_4$ , with the Teflon<sup>®</sup> in the system. Again, no significant differences could be detected in the solvents tested. No difficulty was encountered in removing  $N_2O_4$  from the system when there was only metal or hard parts exposed, but the addition of the Teflon<sup>®</sup> created an unexpected problem.

The compatibility of hard parts with solvents was considered, since titanium stress corrosion is a serious problem in the Apollo propellant tanks. Therefore, this part of the study was included to alleviate the possibility of any of the flush candidates adding to this problem. Also, many bromo and fluoro compounds were added to the list of candidate solvents since chloride ion contamination is thought to be a causative factor in this stress corrosion.

Some suspicion of corrosion was aroused when close inspection of the titanium alloy filings used in the nitrogen tetroxide flushing experiments showed a change from a bright and shiny surface to a dull green color. An x-ray analysis of these filings was made, but the physical configuration was such that no information was obtained. Therefore, a series of tests was set up for the nitrogen tetroxide flushing candidates. Several 3 x 1/2-inch specimens were cut from the propellant tank metal (Ti-Al alloy) and placed in a 125-ml distillation flask along with 70 ml of solvent and refluxed. An equal number of specimens was placed in a flask with a 50/50 mixture of solvent and nitrogen tetroxide. A blank specimen was placed in  $N_2O_4$ , by itself and with the mixtures, and stored at room temperature for 7 days. All specimens were exposed to liquid and vapor for the same period of time. They were weighed before and after exposure and microscopically inspected.

The tests provided little information, probably due to the short exposure time. The weight change of the specimens was within the range of error of the balance.

In addition to examining the behavior of the candidate solvents on soft and hard parts, environmental changes such as elevated temperature and longer soak times were considered. The curves in Figure 1-8 show the effect of soak time and temperature in removing the  $N_2O_4$  from the system. Increasing the soak time for each flush from 1 to 30 minutes increased the amount of  $N_2O_4$  removed from the system. The tests carried out at the higher temperature using carbon tetrachloride affected an increase in the removal of  $N_2O_4$  from the system. The carbon tetrachloride was heated to 75° C by placing an electric heat tape around the solvent feed reservoir. The  $CCl_4$  was fed to

the test chamber at the above temperature, but when it was drained, 30 minutes later, it was only 5 degrees above ambient. Even though the average temperature was only slightly above ambient, more  $N_2O_4$  was removed from the system than at ambient.

The results for the removal of  $N_2O_4$  from the system by various solvents are summarized by the curves shown in Figure 1-9. Figure 1-10 shows the evaluation of a mixture of solvents in removing  $N_2O_4$  from the system. All of the solvent mixtures were 50/50 volume percent. No difference was detected in the efficiency of the solvent since the amount of  $N_2O_4$  remaining in the soft parts was essentially the same for all solvents. Table 1-III summarizes the results of the removal of nitrogen tetroxide from Teflon<sup>®</sup> TFE by the various solvents.

#### F. Evaluation of Solvents for Aerozine-50 Decontamination

The apparatus used in this study is shown in Figure 1-4. Approximately one-third of the test chamber was filled with Ti-Al shavings. The elastomers used were 5-1/2" x 1/2" x 1/32" strips of Rulon and Stillman SR634-70 rubber. The basic decontamination procedure used is briefly described. The elastomers were immersed for a minimum of 24 hours before testing. The contaminated samples were weighed, placed in the test chamber, and one milliliter of A-50 was also added. The test chamber was agitated for about 2 minutes before proceeding with the flush. This was done to spread the A-50 as much as possible. The results of the tests are shown by the curves in Figures 1-11 and 1-12. Figure 1-11 shows the solvent absorption curves using halogenated solvents. Figure 1-12 shows curves for methyl and ethyl alcohol, hexane, and pentane flushing.

Stillman rubber and Rulon rapidly absorb A-50, but desorption is difficult to bring about. It follows that the key to reduction of contamination to a given desired level may be the removal of A-50 from the system's soft parts. The first method tried in determining the residual contamination level remaining in the soft parts after flushing and in blanks was to leach them with water. This method was unsuccessful; leaching with dilute acid gave only a slight improvement. It was found that refluxing the contaminated soft parts in dilute acid for a period of 24 hours was a satisfactory procedure. The information presented in the first series of runs was inconclusive because the A-50 absorbed was not satisfactorily determined.

The curves in Figures 1-13 and 1-14 show the decontamination of the system using alcohols and other oxygenated compounds at room temperature. Inspection of these figures shows the alcohols are the best solvents for removing the fuel from the test apparatus. The curves in 1-15, 1-16, and 1-17 were developed from tests using various alcohols at elevated

temperature. The curves show that an increase in temperature improves the removal of fuel from the system and the elastomers. The results are summarized in Table 1-IV for the Aerozine-50 decontamination investigation.



G. Tables

TABLE 1-I

Explosion Tests - Nitrogen Tetroxide Mixtures

<u>Test Solvent</u>	<u>Test Results</u>
1. Trichloroethylene - 200 ml	High order explosion
2. 2,2-Dichloro-1,1-difluoroethyl methyl ether - 100 ml	High order explosion
3. Bromodichloromethane - 100 ml	No explosion
4. Tribromofluoromethane - 50 ml	No explosion
5. Freon <sup>®</sup> 11 (Fluorotrichloromethane - 100 ml	No explosion
6. Dibromochloromethane - 100 ml	High order explosion
Dibromochloromethane - 100 ml	No explosion
Dibromochloromethane - 100 ml	No explosion
7. 1,1-Dibromo-2,2,2-trifluoroethane - 100 ml	No explosion
8. Freon <sup>®</sup> 112 (mixed isomers of difluoro-tetrachloroethane) - 100 ml	No explosion
9. Freon <sup>®</sup> C-318 (Cyclo(CF <sub>2</sub> ) <sub>4</sub> - 50 ml	No explosion
10. Dibromodifluoromethane - 50 ml	No explosion
11. 50 Vol. % Freon <sup>®</sup> 112 - 100 ml 50 Vol. % Bromochloromethane	No explosion

TABLE 1-II

Explosion Tests - Aerozine-50 Mixtures

<u>Test Mixture</u>	<u>Results</u>
1. Methanol	Ignition. No detonation Sample cup intact
2. Ethanol	Ignition. No detonation Sample cup intact
3. n-Hexane	Ignition. No detonation Sample cup intact
4. Aerofuel-50 <sup>®</sup>	Ignition. No detonation Sample cup intact
5. Aerofuel-50 <sup>®</sup> - Methanol	Ignition. No detonation Sample cup intact
6. Aerofuel-50 <sup>®</sup> - Ethanol	Ignition. No detonation Sample cup intact
7. Aerofuel-50 <sup>®</sup> - n-Hexane	Ignition. No detonation Sample cup intact
8. Aerofuel-50 <sup>®</sup> - Methylene chloride	Ignition. No detonation Sample cup intact
9. Aerofuel-50 <sup>®</sup>	Ignition. No detonation Sample cup intact
10. Aerofuel-50 <sup>®</sup> - Chloroform	Ignition. No detonation Sample cup intact
11. Aerofuel-50 <sup>®</sup> - Freon <sup>®</sup> 11	Ignition. No detonation Sample cup intact
12. Aerofuel-50 <sup>®</sup> - Freon <sup>®</sup> 113	Ignition. No detonation Sample cup intact
13. Aerofuel-50 <sup>®</sup> - Bromochloromethane	Ignition. No detonation Sample cup intact

TABLE 1-II (Cont'd)

Liquid Tested

Same procedure as above except the blasting cap was placed in the liquid portion of the mixture.

Test Mixture

Results

- |   |                                     |
|---|-------------------------------------|
| 1. Aerofuel-50 <sup>®</sup>                         | Low order explosion.<br>No ignition |
| 2. Aerofuel-50 <sup>®</sup> - Freon <sup>®</sup> 11 | Low order explosion.<br>No ignition |
| 3. Aerofuel-50 <sup>®</sup> - Methylene chloride    | Low order explosion.<br>No ignition |
| 4. Aerofuel-50 <sup>®</sup> - Bromochloromethane    | Low order explosion.<br>No ignition |

TABLE 1-III

Removal of N<sub>2</sub>O<sub>4</sub> From Teflon<sup>®</sup> TFE

Solvent	Run No.	Total Soak Time (Min.)	Nitrogen Tetroxide			
			Absorbed (g)	Remaining (g)	Removed (g)	% Removed
CCl <sub>4</sub>	4 C1	20	0.7194	0.512	0.207	28.8
	4 C2	120	0.7250	0.348	0.377	52.0
	5 C3	120 at 75°C	0.7687	0.336	0.433	56.3
BRHCCl <sub>2</sub>	4 K1	120	0.7309	0.252	0.479	65.5
	5 K2	120 at 90°C	0.7181	0.348	0.370	51.6
BR <sub>2</sub> CHCF <sub>3</sub>	4 L1	120	0.7064	0.368	0.338	48.0
Cl <sub>2</sub> CHCF <sub>3</sub>	4 AAl	120	0.5307	0.172	0.359	67.6
H <sub>2</sub> CBR <sub>2</sub>	4 BB1	120	0.6915	0.272	0.420	60.8
BR <sub>2</sub> CF <sub>2</sub>	4 CC1	120	0.7428	0.260	0.482	65.0
50% H <sub>2</sub> CBRCl	4 E1	20	0.7220	0.434	0.288	39.9
50% Freon 112						
50% CHCl <sub>3</sub>	4 F1	20	0.7223	0.460	0.262	36.3
50% Freon 11						
50% CCl <sub>4</sub>	4 G1	20	0.7161	0.416	0.300	42.0
50% Freon 11						
50% CCl <sub>4</sub>	4 H1	20	0.7203	0.446	0.276	38.4
50% Freon 112						
50% CHCl <sub>3</sub>	4 I1	20	0.9626	0.400	0.560	57.2
50% Freon 112						
50% Freon 11	4 J1	20	0.6508	0.440	0.211	32.5
50% Freon 112						

TABLE 1-IV

## Removal of Aerozine-50 from Soft Parts

<u>Solvent</u>	<u>Run Number</u>	<u>Total Soak Time (Min.)</u>	<u>Aerofuel 50<sup>®</sup></u>			
			<u>Absorbed (g)</u>	<u>Remaining (g)</u>	<u>Removed (g)</u>	<u>% Removed</u>
Methanol	1 M3	60	0.7858	0.380	0.406	51.6
	2 M4	60 at 50°C	0.9190	0.192	0.727	79.1
Ethanol	1 N2	60	0.9536	0.413	0.541	56.7
	2 N3	60 at 65°C	0.8534	0.175	0.678	79.5
Isopropanol	1 V1	60	0.9335	0.451	0.462	49.5
	2 V2	60 at 80°C	0.9015	0.107	0.794	88.0
Secondary Butanol	1 X1	60	0.9395	0.430	0.509	54.1
	2 X2	60 at 100°C	0.9250	0.126	0.799	86.4
Acetone	1 Y1	60	0.8909	0.352	0.539	60.5
1,4-Dioxane	1 Z1	60	1.9405	0.207	1.733	89.2
1,2-Butylene Oxide	1 1	60	0.8316	0.241	0.591	71.0

H. Figures

FIGURE 1-1  
APPARATUS FOR DECONTAMINATION:  
SYSTEM A

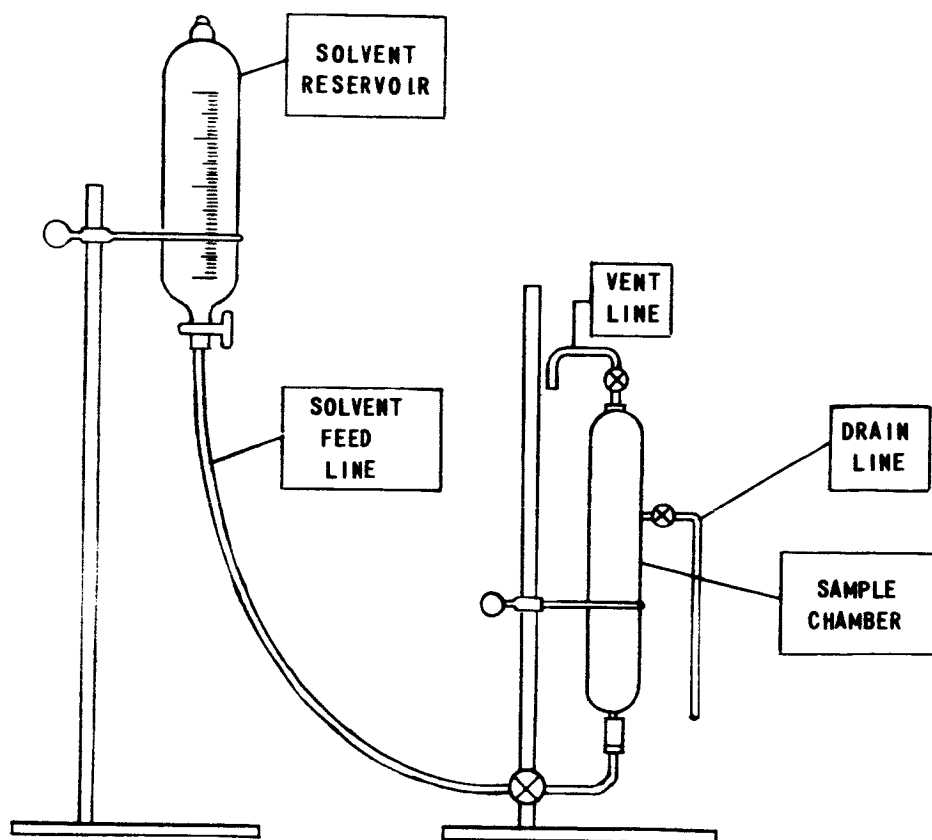


Figure 1-2

Apparatus for Decontamination:

System B

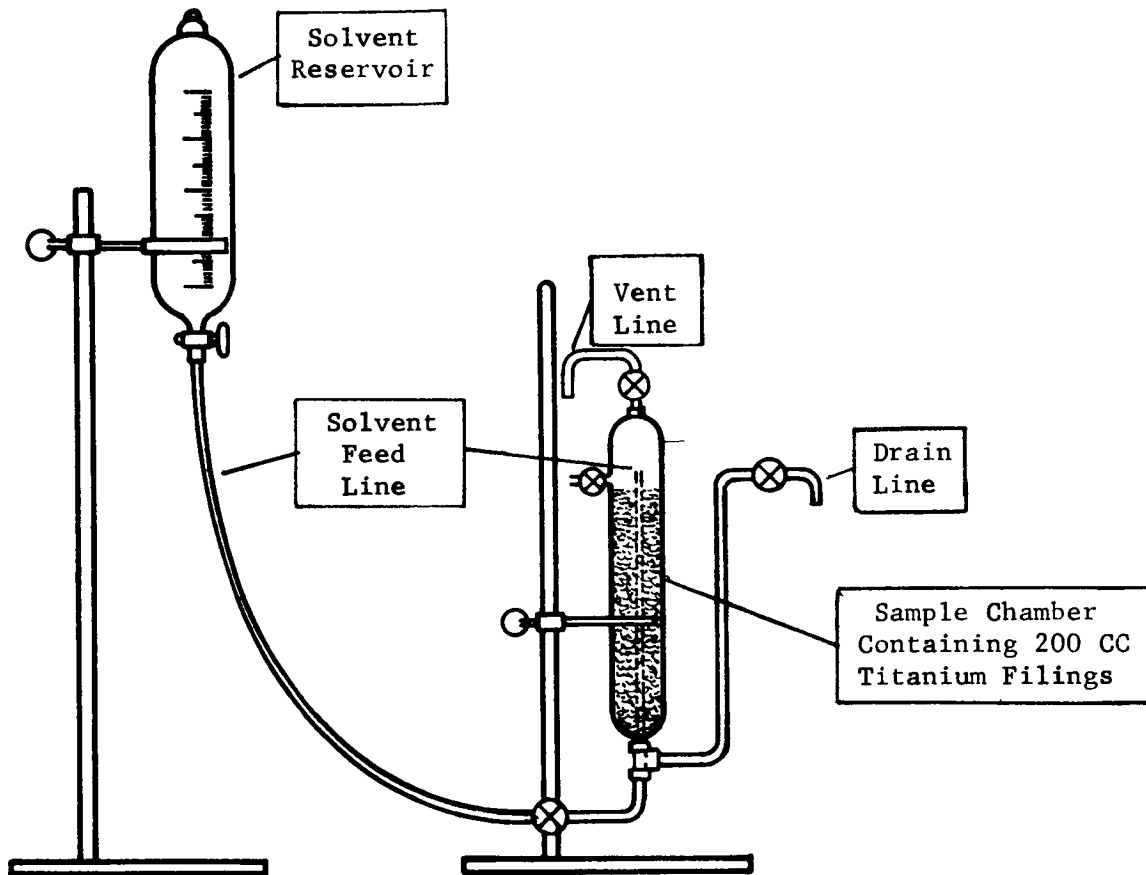


Figure 1-3

Apparatus for Decontamination:

System C

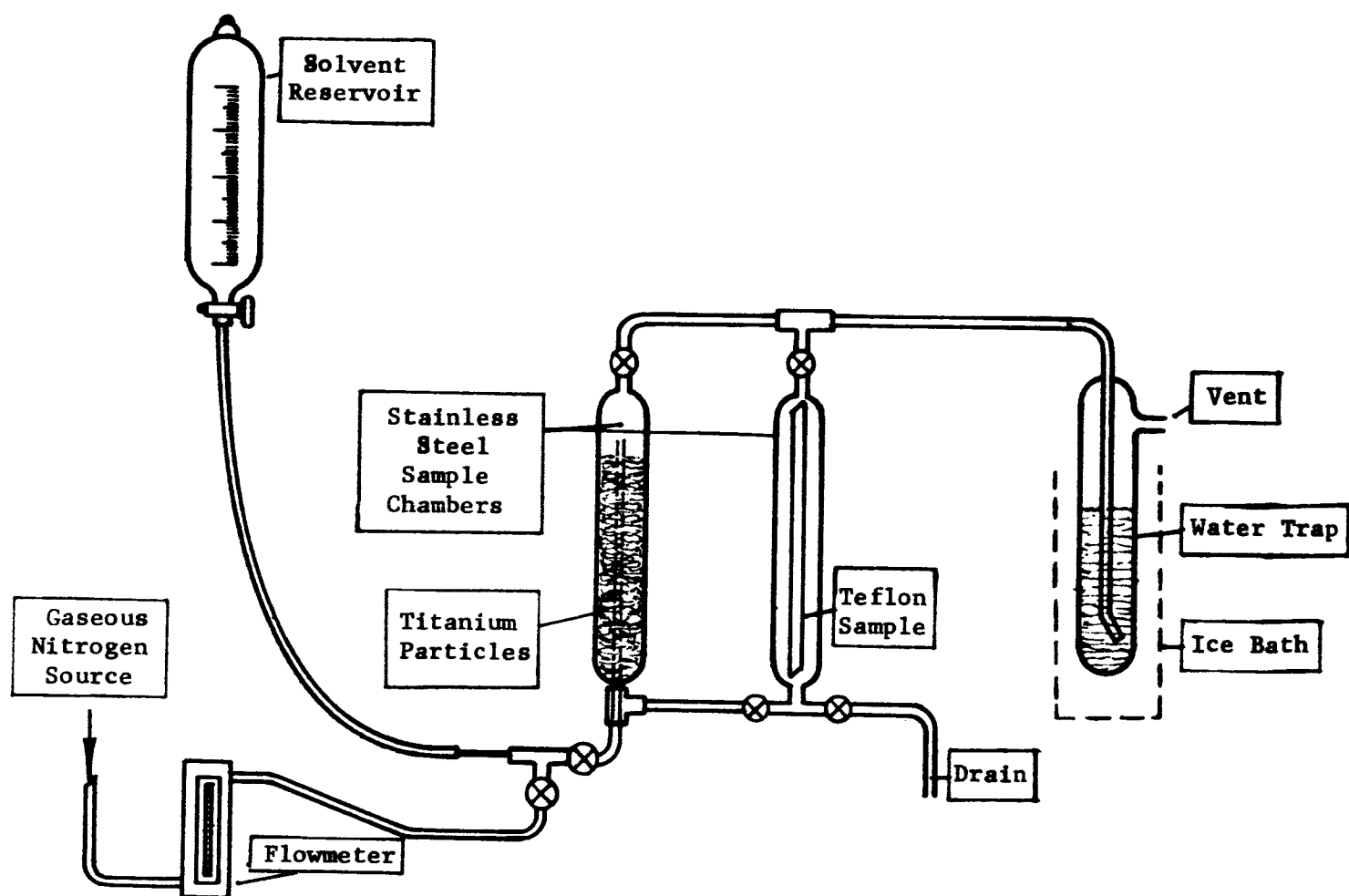




Figure 1-4

Apparatus for Decontamination:

System D

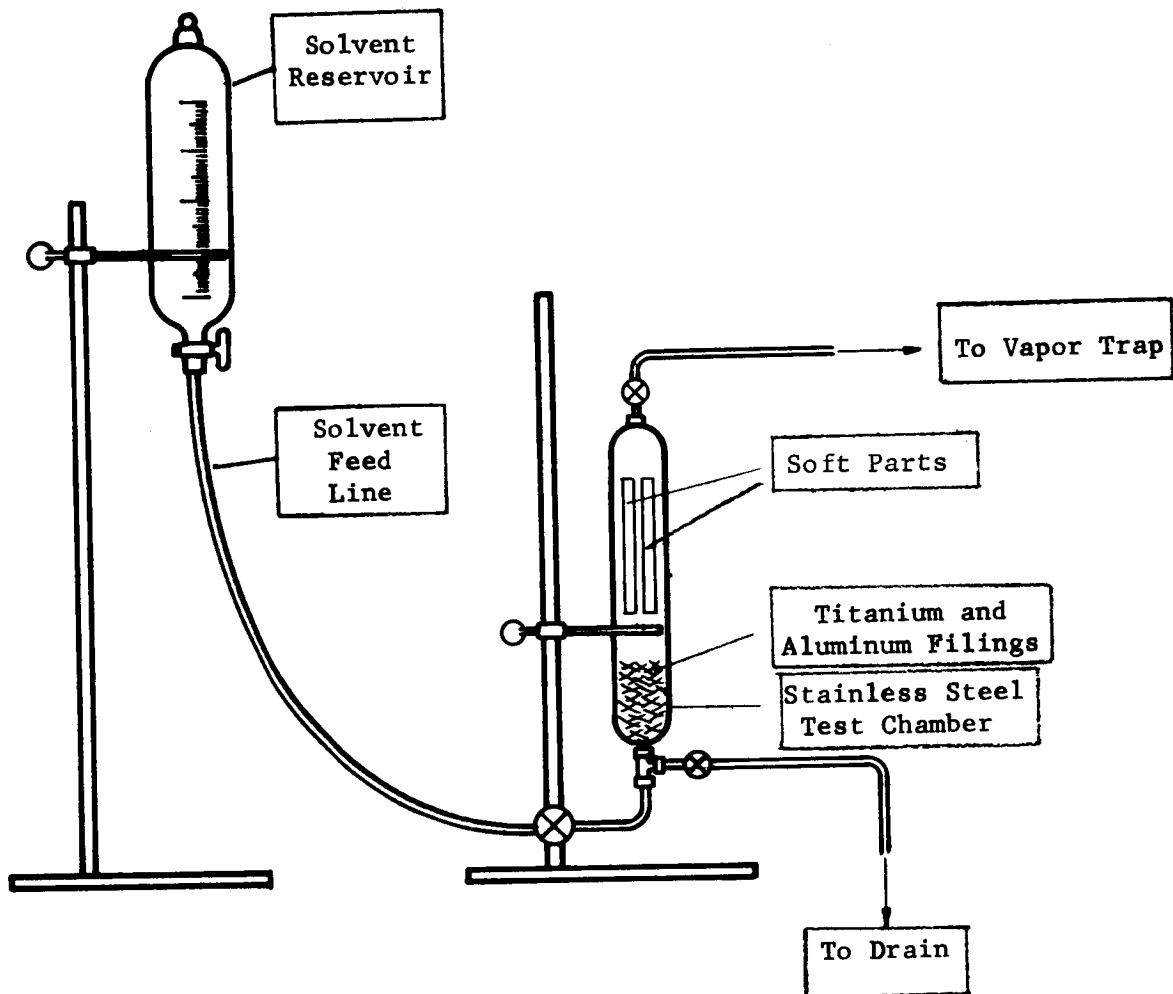


Figure 1-5

REMOVAL OF  $N_2O_4$  FROM SYSTEM "B"  
(System B is shown in Fig. 1-2. No Al fillings.)

BY

1. FILL-EMPTY METHOD  
Soak Time - 1 min.  
No. of Flushes - 4
2. CONTINUOUS FLUSH METHOD  
Soak Time - 1 min.  
No. of Displacements - 4

Volume of Solvent each Flush or Displacement: 250 ml.  
Total  $N_2O_4$  in System at Start: 1.4 gms.

$N_2O_4$  Concentration in Solvent Effluent (ppm)

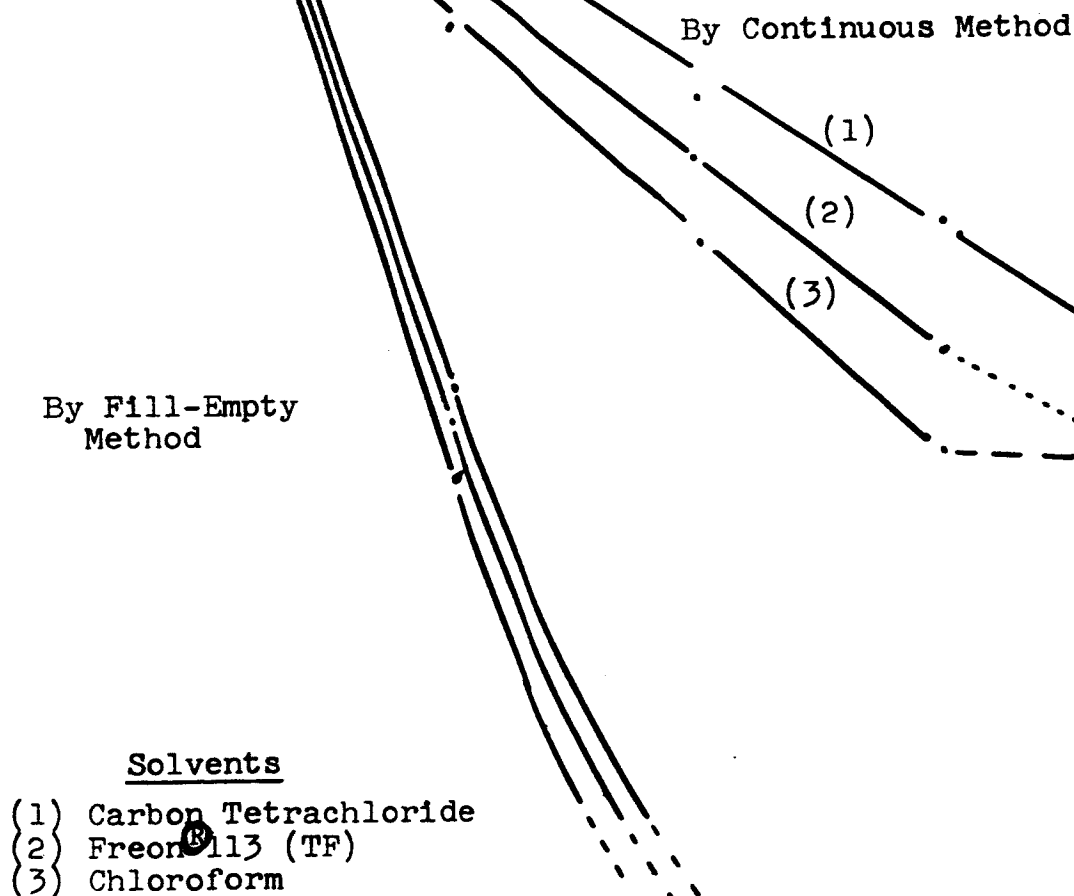
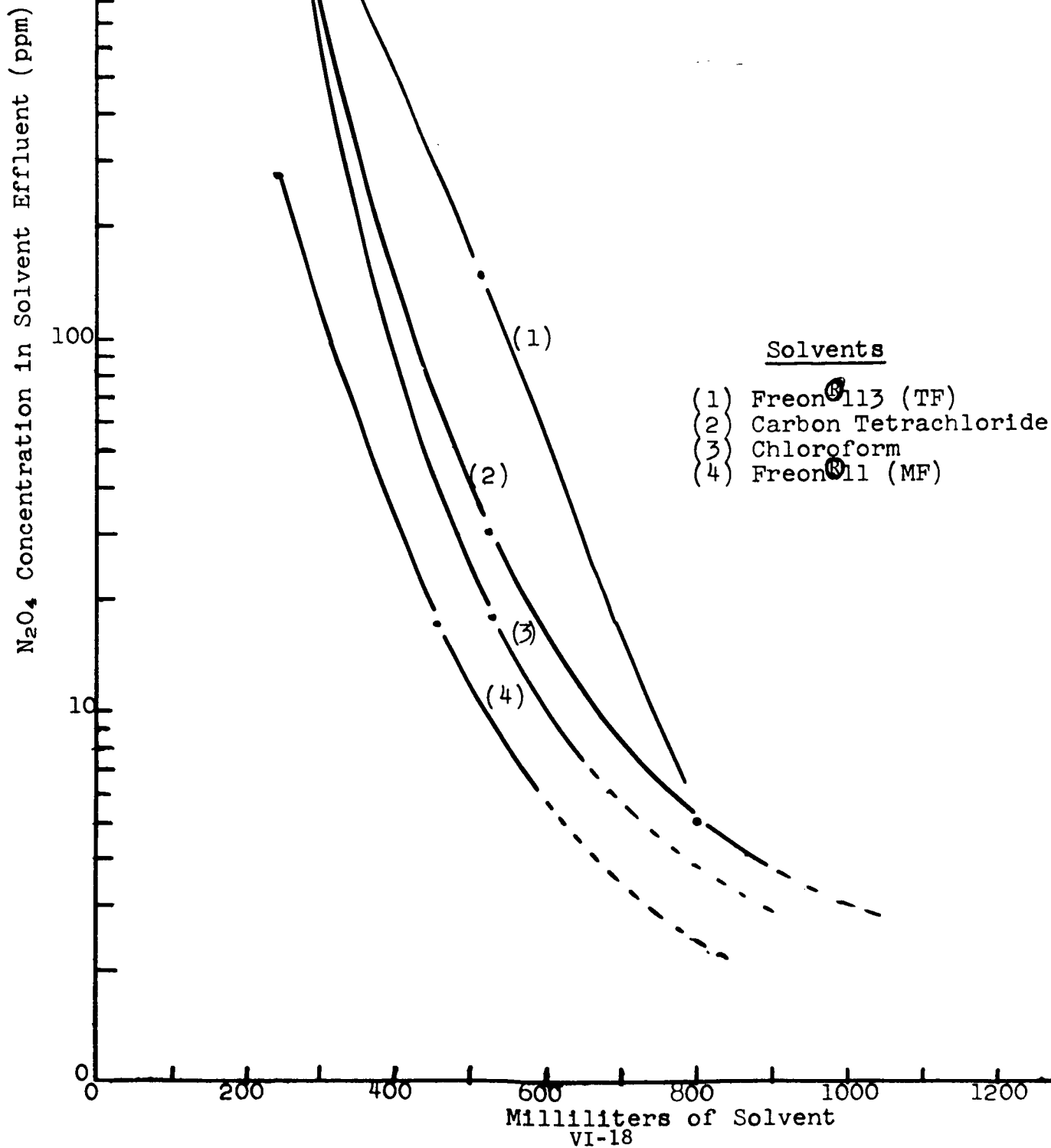


Figure 1-6

REMOVAL OF  $N_2O_4$  FROM SYSTEM "B"  
(System B is shown in Fig. 1-2)  
BY  
FILL-EMPTY METHOD

Soak Time - 1 Min.  
No. of Flushes - 4  
Volume of Solvent Each Flush - 250 ml.  
Total  $N_2O_4$  in System at Start - 1.4 gms



10,000

Figure 1-7

REMOVAL OF  $N_2O_4$  FROM SYSTEM "C"  
(System C is shown in Fig. 1-3)

BY  
FILL-EMPTY METHOD

Soak Time - 5 min.  
No. of Flushes - 4  
Volume of Solvent Each Flush - 500 ml  
Total  $N_2O_4$  in System at Start - 2.1 gms

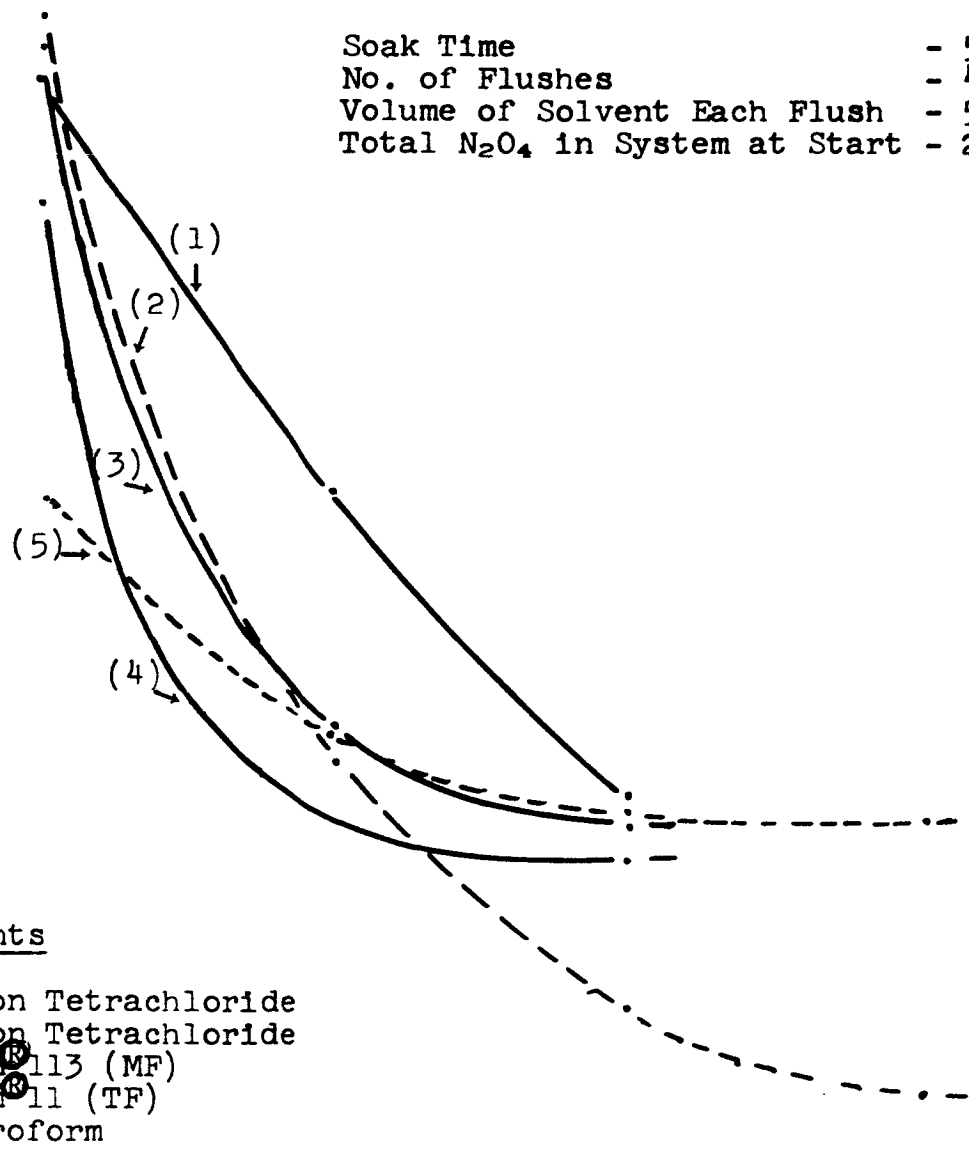
$N_2O_4$  Concentration (ppm) in Solvent Effluent

1,000

100

10

0



Solvents

- (1) Carbon Tetrachloride
- (2) Carbon Tetrachloride
- (3) Freon 113 (MF)
- (4) Freon 11 (TF)
- (5) Chloroform

Milliliters of Solvent

10,000

Figure 1-8

REMOVAL OF  $N_2O_4$  FROM SYSTEM "D"  
(System D is shown in Fig. 1-4)

BY

FILL-EMPTY METHOD

No. of Flushes - 4  
Volume of Solvent Each Flush - 250 ml.  
Total  $N_2O_4$  in System at Start - 2.1 gm.  
Soft Parts - Teflon® (TFE)

$N_2O_4$  Concentration (ppm) in Solvent Effluent

1,000

100

10

0

250

500

750

1000

Milliliters of Solvent  
VI-20

Solvents

- (1)  $CCl_4$  (30 min. each flush)
- (2)  $CCl_4$  (30 min. each flush at 75°C.)
- (3)  $CCl_4$  (5 min. each flush)
- (4)  $CCl_4$  (1 min. each flush)

(4)

(3)

(2)

(1)

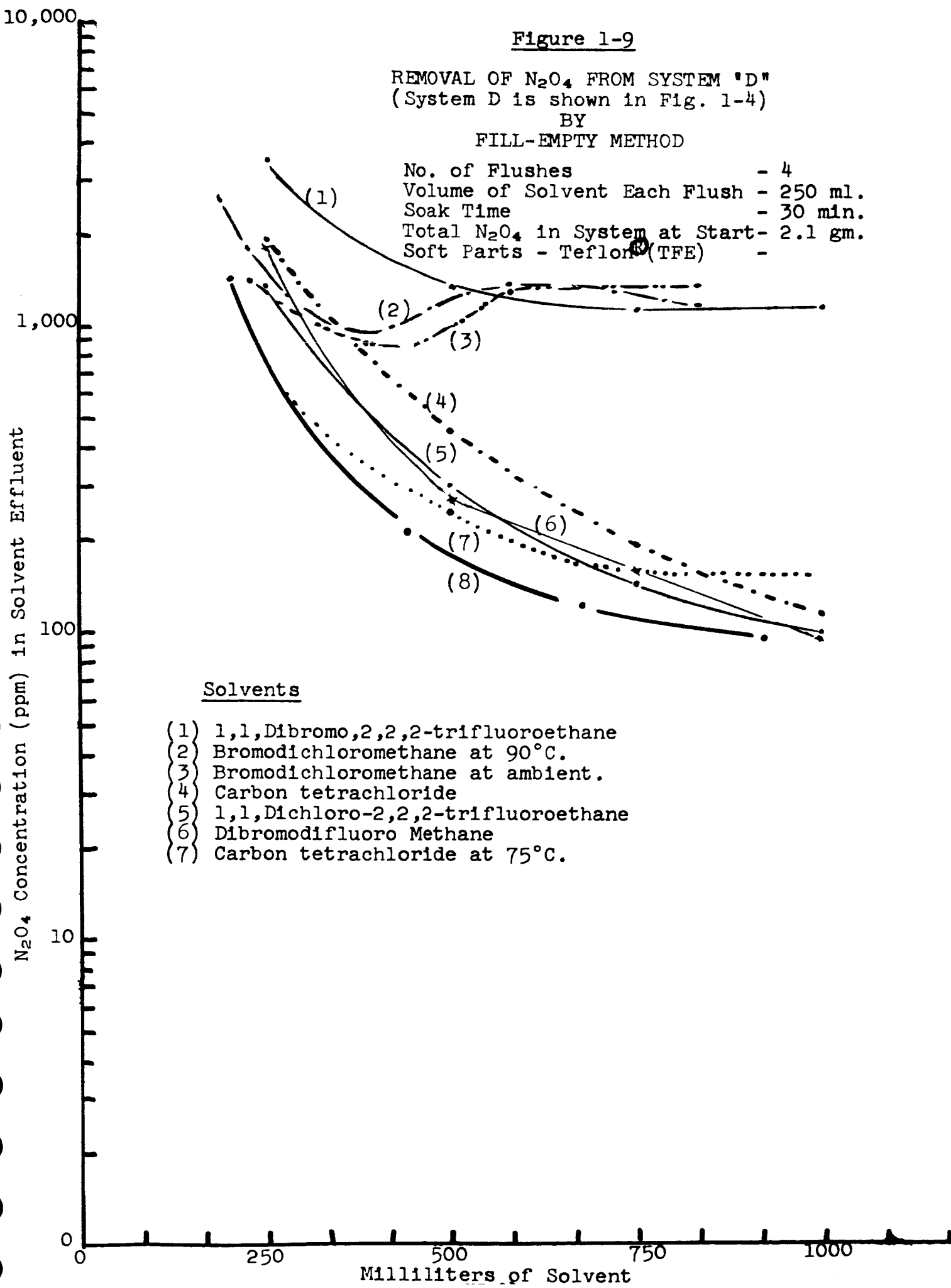
Figure 1-9

REMOVAL OF  $N_2O_4$  FROM SYSTEM "D"  
(System D is shown in Fig. 1-4)

BY

FILL-EMPTY METHOD

No. of Flushes - 4  
Volume of Solvent Each Flush - 250 ml.  
Soak Time - 30 min.  
Total  $N_2O_4$  in System at Start - 2.1 gm.  
Soft Parts - Teflon (TFE) -



10,000

Figure 1-10

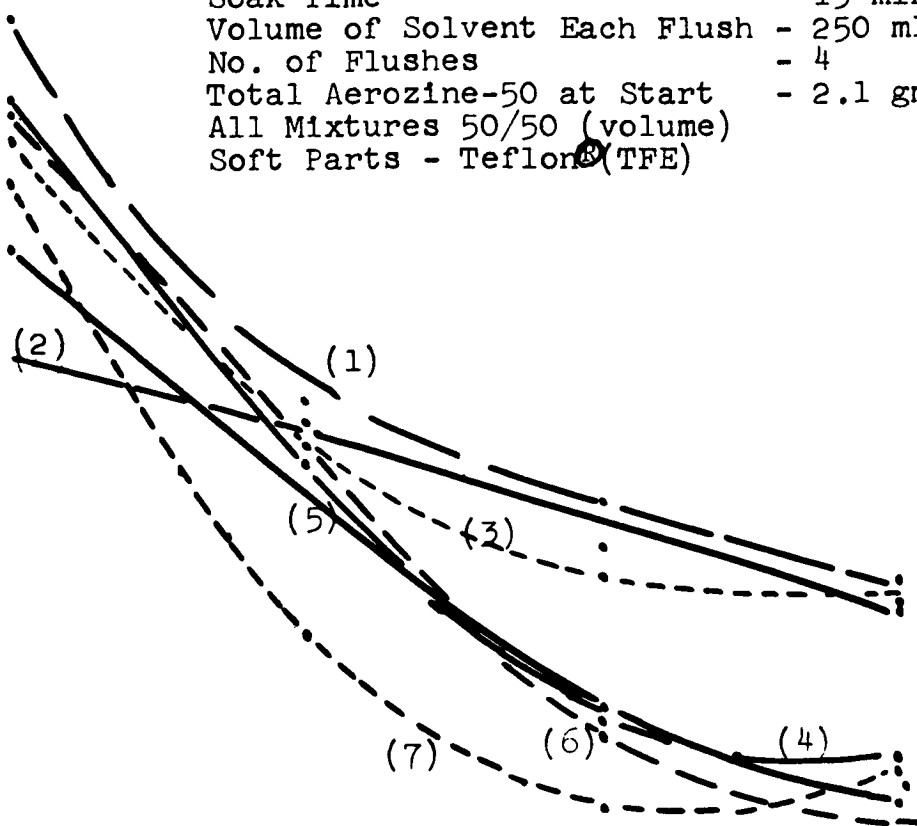
REMOVAL OF  $N_2O_4$  FROM SYSTEM "D"  
(System D is shown in Fig. 1-4)

BY

FILL-EMPTY METHOD

Soak Time - 15 min.  
Volume of Solvent Each Flush - 250 ml.  
No. of Flushes - 4  
Total Aerozine-50 at Start - 2.1 gms.  
All Mixtures 50/50 (volume)  
Soft Parts - Teflon® (TFE)

$N_2O_4$  Concentration (ppm) in Solvent Effluent



### Solvents

- (1) Freon® 112 and Carbon tetrachloride
- (2) Freon® 112 and Bromochloro methane
- (3) Freon® 112 and Freon® 11
- (4) Carbon tetrachloride
- (5) Freon® 11 and chloroform
- (6) Freon® 11 and carbon tetrachloride
- (7) Freon® 112 and Chloroform

Milliliters of Solvent

Figure 1-11

REMOVAL OF AEROZINE-50 FROM SYSTEM "D"  
(System C is shown in Fig. 1-4)

BY

FILL-EMPTY METHOD

No. of Flushes - 4  
Volume of Solvents Each Flush - 250 ml.  
Soak Time - 5 min.  
Total Aerozine-50 at Start - 1.70 gms.  
Soft Parts - Butyl Rubber and Rulon

Aerozine-50 Concentration (ppm) in Solvent Effluent

- Solvents
- (1) Chloroform
  - (2) Methylene Chloride
  - (3) Freon 11 (MF)
  - (4) Freon 113 (TF)
  - (5) Carbon Tetrachloride

Milliliters of Solvent

0

250

500

750

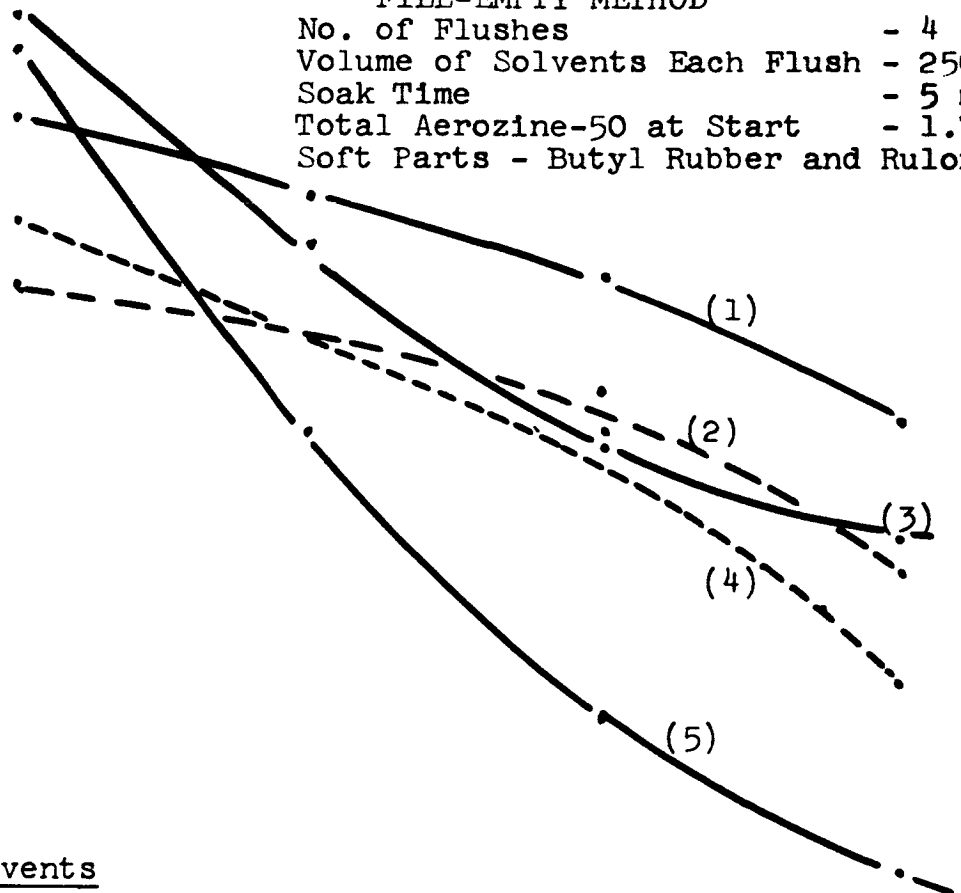
1000

10

100

1,000

10,000





10,000

Figure 1-12

REMOVAL OF AEROZINE-50 FROM SYSTEM "D"  
(System D is shown in Fig. 1-4)

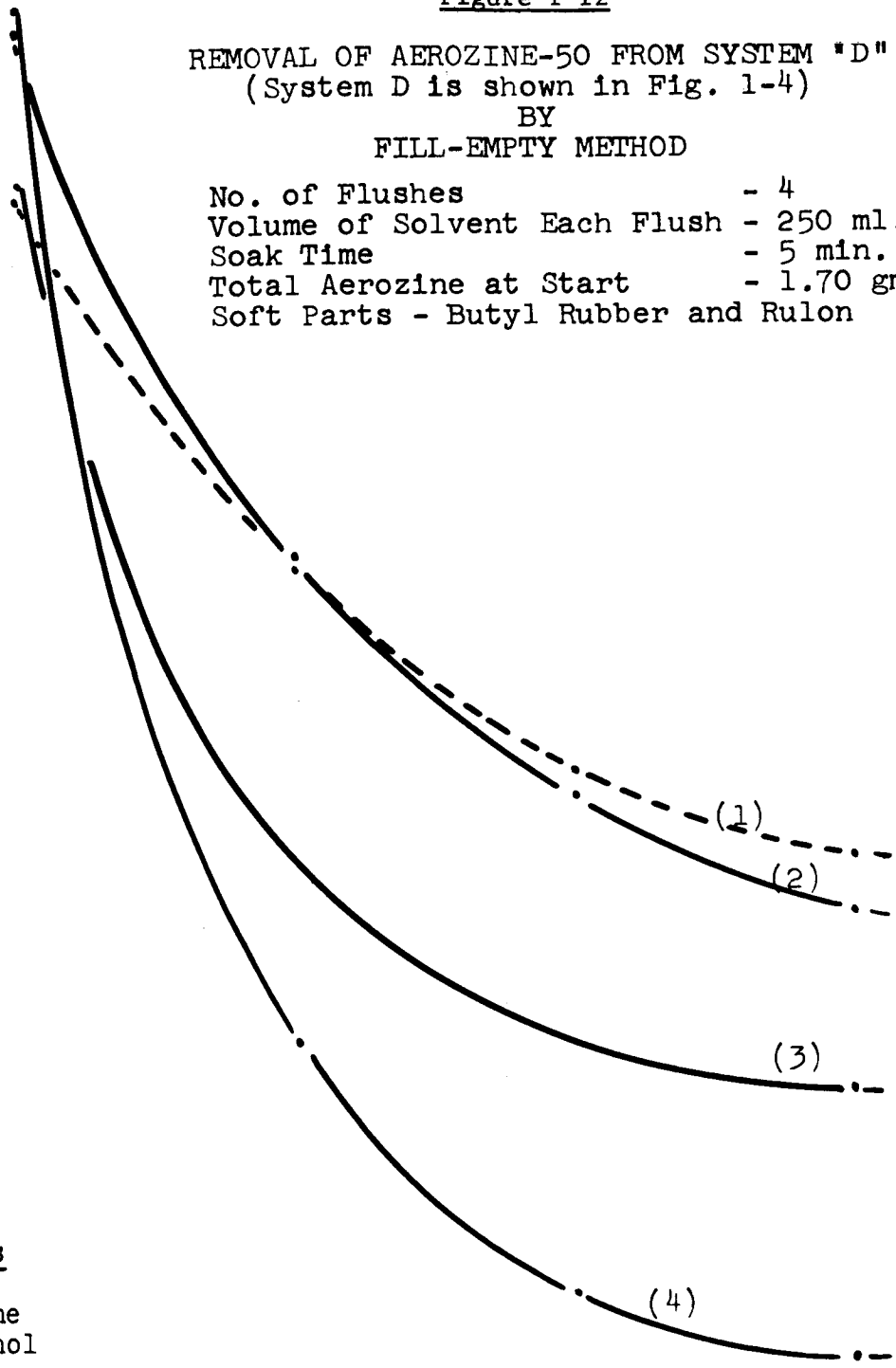
BY

FILL-EMPTY METHOD

No. of Flushes - 4  
Volume of Solvent Each Flush - 250 ml.  
Soak Time - 5 min.  
Total Arozine at Start - 1.70 gms.  
Soft Parts - Butyl Rubber and Rulon

Aerozine-50 Concentration (ppm) in Solvent Effluent

- Solvents
- (1) Hexane
  - (2) Ethanol
  - (3) Pentane
  - (4) Methanol



10,000

Aerozine-50 Concentration (ppm) in Solvent Effluent

1,000

100

10

0

250

500

750

1000

Milliliters of Solvent

VI-25

Figure 1-13

REMOVAL OF AEROZINE-50 FROM SYSTEM "D"  
(System D is shown in Fig. 1-4)

BY

FILL-EMPTY METHOD

No. of Flushes - 4  
Volume of Solvent Each Flush - 250 ml.  
Soak Time - 15 min.  
Total Aerozine at Start - 1.70 gms.  
Soft Parts - Stillman Rubber and Rulon

- Solvents
- (1) Ethanol
  - (2) Isopropyl Alcohol
  - (3) Secondary Butyl Alcohol
  - (4) Methanol

(1)

(2)

(3)

(4)

Aerozine-50 Concentration (ppm) in Solvent Effluent

10,000

Aerozine-50 Concentration (ppm) in Solvent Effluent

1,000

100

10

0

250

500

750

1000

Milliliters of Solvent

VI-26

Figure 1-14

REMOVAL OF AEROZINE-50 FROM SYSTEM "D"  
(System D is shown in Fig. 1-4)

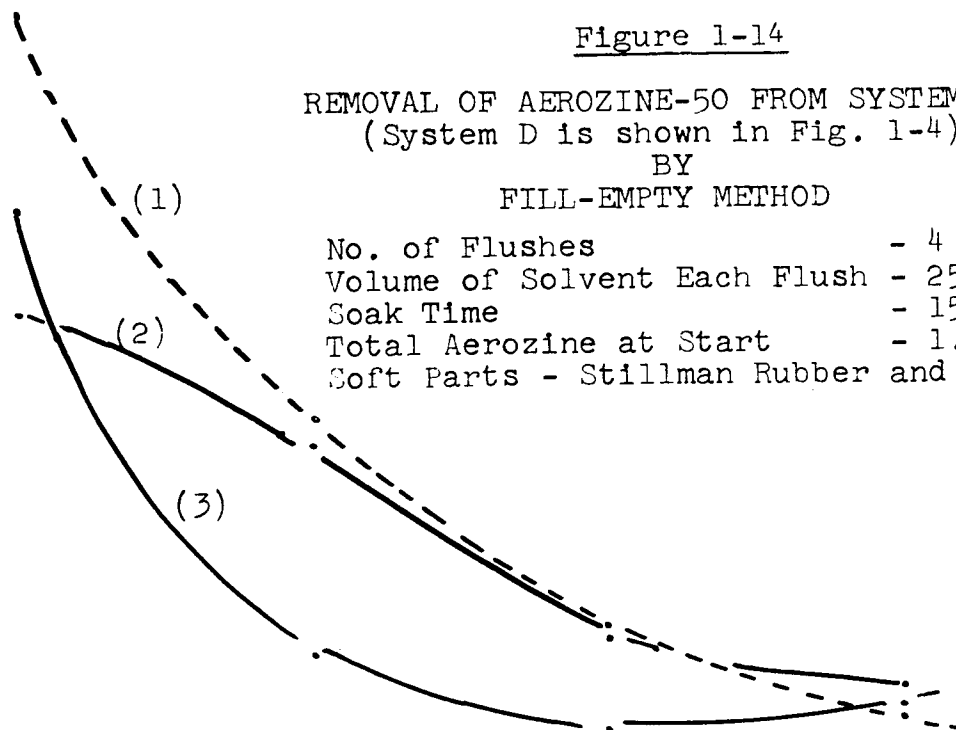
BY

FILL-EMPTY METHOD

No. of Flushes	- 4
Volume of Solvent Each Flush	- 250 ml.
Soak Time	- 15 min.
Total Aerozine at Start	- 1.70 gms.
Soft Parts - Stillman Rubber and Rulon	

Solvents

- (1) Butylene Oxide
- (2) Dioxane
- (3) Acetone



10,000

Aerozine-50 Concentration (ppm) in Solvent Effluent

1,000

100

10

0

250

500

750

1000

Milliliters of Solvent

Figure 1-15

REMOVAL OF AEROZINE-50 FROM SYSTEM "D"  
(System D is shown in Fig. 1-4)

BY

FILL-EMPTY METHOD

No. of Flushes - 4  
Volume of Solvent Each Flush - 250 ml.  
Soak Time - 30 min.  
Total Aerozine at Start - 1.70 gms.  
Soft Parts - Stillman Rubber and Rulon

(1)

(2)

(3)

(4)

Solvents

- (1) Ethanol at 65°C.
- (2) Isopropyl Alcohol at 80°C.
- (3) Methanol at 50°C.
- (4) Sec-Butyl Alcohol at 100°C.

10,000

Figure 1-16

REMOVAL OF AEROZINE-50 FROM SYSTEM "D"  
(System D is shown in Fig. 1-4)

BY

FILL-EMPTY METHOD

No. of Flushes - 4  
Volume of Solvent Each Flush - 250 ml.  
Soak Time at Elevated Temp. - 30 min.  
Soak Time at Ambient Temp. - 15 min.  
Total Aerozine at Start - 1.70 gms.  
Soft Parts - Stillman Rubber and Rulon

Aerozine-50 Concentration (ppm) in Solvent Effluent

1,000

100

10

Solvent

- (1) Ethanol at ambient
- (2) Isopropanol at 80°C.
- (3) Isopropanol at ambient
- (4) Ethanol at 65°C.

(1)

(2)

(3)

(4)

Milliliters of Solvent

1000

10,000

Figure 1-17

REMOVAL OF AEROZINE-50 FROM SYSTEM "D"  
(System D is shown in Fig. 1-4)

BY

FILL-EMPTY METHOD

No. of Flushes - 4  
Volume of Solvent Each Flush - 250 ml.  
Soak Time at Elevated Temp. - 30 min.  
Soak Time at Ambient Temp. - 15 min.  
Total Arozine at Start - 1.70 gms.  
Soft Parts - Stillman Rubber and Rulon

Aerozine-50 Concentration (ppm) in Solvent Effluent

1,000

100

10

Solvent

- (1) Methanol at 50°C.  
(2) Secondary Butyl Alcohol at 100°C.  
(3) Secondary Butyl Alcohol at ambient  
(4) Methanol at ambient

(1)

(2)

(3)

(4)

0

250

500

750

1000

Milliliters of Solvent

## VII. UNITS 1a AND 1b - SOLVENT REGENERATION TECHNIQUES

### A. Summary

1. Hydrazine and unsymmetrical dimethyl hydrazine (UDMH) may be efficiently removed from polar (methanol) or non-polar (Freon<sup>®</sup> 113) solvents by cation exchange resins (Dowex<sup>®</sup> 50W-X8, 50-100 mesh, H<sup>+</sup>). This is the recommended procedure.
2. Silica gel, water-swollen, and containing dissolved sodium hydroxide, is a very effective extractant. It appears to offer no particular problem. This appears the most satisfactory of the column extraction methods for N<sub>2</sub>O<sub>4</sub>.
3. Water extraction is very effective for N<sub>2</sub>O<sub>4</sub>.
4. Blowing-out of N<sub>2</sub>O<sub>4</sub> by use of air or nitrogen reduces acids to low levels, with residuals being components other than N<sub>2</sub>O<sub>4</sub>. Blowing-out equipment could be constructed and operated quite simply. Blowing out followed by extraction with caustic laden silica gel is the recommended procedure.

As a portion of the total effort under this contract, it was deemed desirable to develop methods for removal of active fuel and oxidizer agents, viz. hydrazines and nitrogen tetroxide, from flushing solvents. The purposes are twofold: (1) to permit repeated recycling of solvent as flush to propulsion system, and (2) to minimize disposal problems of contaminated solvents.

Several ideas were considered in the original contract proposal which involved such extraction techniques as ion exchange, liquid-liquid extraction, adsorption, and gel-water extraction. This report discusses the experimental results of these studies and includes comments on additional concepts which were tested.

### B. Experimental and Results

#### 1. Source of Materials

The solvents used were commercial grade methanol and Freon<sup>®</sup> 113 obtained from du Pont. They were used as received. Preliminary attempts to use Freon<sup>®</sup> 11 were discontinued because its high volatility made laboratory operations without special equipment very difficult.

Anhydrous hydrazine and unsymmetrical dimethyl hydrazine (UDMH) were obtained from Olin and FMC respectively. These were transferred by pipet into clean bottles and diluted with solvent to give approximately 500 ppm solutions. Nitrogen tetroxide (N<sub>2</sub>O<sub>4</sub>) was obtained in a 5-lb. cylinder from Matheson. A small volume was transferred to a chilled bottle and diluted with cold Freon<sup>®</sup> 113 to give a stock solution which was diluted to 500 ppm as needed.

The two major resins used were Dowex<sup>®</sup> 50W-X8, 50-100 mesh, H<sup>+</sup> form (Lot 07285-W2) and Dowex<sup>®</sup> 21K, 50-100 mesh, Cl<sup>-</sup> form (Lot 03124-668). One ml of the resin as received was washed into a column made by putting a glass-wool plug in a 2 ml graduated pipet. The 1 ml bed of resin had a height of about 9.7 cm and a cross-sectional area of approximately 0.1 cm<sup>2</sup>.

The molecular sieves were grade 5A from Linde. The silica gel was grade 42 from Davison, 6-16 mesh. The desired water content was achieved by placing the adsorbents and water in separate shallow dishes in a desiccator and allowing sufficient time for equilibration. In the case of the silica gel containing NaOH, this adsorbent was prepared by immersing silica gel containing about 9% water in a 1 N solution of NaOH.

## 2. Analytical Methods

Both the hydrazines and the N<sub>2</sub>O<sub>4</sub> were determined by acid-base titration. When the solvent was immiscible with water, the titration was carried out in a stirred two-phase system with the electrodes in the water phase. In the case of the hydrazines, it was necessary to perform the titration on the recording titrator since the break was quite shallow and tended to vary in pH with concentration and solvent ratio. Equilibrium was obtained relatively rapidly. The N<sub>2</sub>O<sub>4</sub> solutions were titrated to pH 7 using a standard pH meter. However, in most cases, they were very slow to come to equilibrium, often requiring at least 15 minutes to obtain a pH of 7 which did not drift. It is not known whether this is a characteristic of the N<sub>2</sub>O<sub>4</sub> or is due to the presence of some trace acidic component in the system. The latter seems more likely.

## 3. Fuel Side

### a. UDMH from Freon<sup>®</sup> 113 by Ion Exchange

The excess water was blown out of the 1 ml column of Dowex<sup>®</sup> 50W, H<sup>+</sup> and a 450 ppm (0.012 N) UDMH in Freon<sup>®</sup> 113 solution was passed through it. The effluent was collected in appropriate cuts and titrated. The first 160 ml contained 4 ppm or less of UDMH. After an additional 30 ml, the concentration was about 100 ppm. There was no observable water phase in any of the cuts. The flow rate was very uneven but averaged roughly 1 ml/minute which is equivalent to 2.5 gpm/sq.ft. or 7.5 gpm/cu.ft.



As a check on the ion exchange capacity of the column, it was regenerated with 5 ml of  $N$  HCl, rinsed and exhausted with a  $NaNO_3$  solution. The effluent was titrated for  $H^+$  giving an exchange capacity of 1.63 meq.

The column was regenerated with 10 ml  $N$  HCl, rinsed, and the UDMH-Freon<sup>®</sup> 113 run repeated. The flow rate was held fairly constant at 1 ml/minute in this run. The effluent concentration is shown in Figure 1a-1. A volume of 150 ml was obtained in which the UDMH concentration was less than 2 ppm and an additional 20 ml at less than 5 ppm, followed by a fairly sharp breakthrough to feed concentration. Thus, in each of these runs the resin is removing approximately  $160 \times 0.012 = 1.9$  meq of UDMH, or slightly more than the exchange capacity. The water-swollen resin apparently has some sorptive capacity for UDMH in the Freon<sup>®</sup> 113 system.

b. UDMH-Hydrazine from Methanol by Ion Exchange

When the information was received that methanol was the current solvent of choice on the fuel side, the above runs were repeated with a UDMH-methanol solution. The column was refilled with new resin and the water was displaced from the resin by a methanol wash prior to the run. The feed solution was a 400 ppm (0.0054  $N$ ) solution of UDMH in methanol. The flow rate varied from 0.5 to 1.0 ml/minute. The first three 100 ml cuts collected contained 2, 4, and 8 ppm UDMH, respectively. After this, the effluent concentration increased to feed concentration within the next 100 ml. The capacity obtained was slightly greater than  $300 \times 0.0054 = 1.6$  meq.

The column was regenerated with 50 ml of  $N/4$  methanolic HCl prepared by adsorbing HCl gas in methanol. The UDMH in the regenerant effluent was estimated, by titration after the addition of excess base, to be 1.6 meq. This determination is subject to considerable error if the base added contains any carbonate.

This regenerated column was again exhausted with the UDMH-methanol solution at a flow rate of about 0.5 ml/minute with the following results:

<u>Cut No.</u>	<u>Volume</u>	<u>Concentration of UDMH</u>
1	250 ml	1.5 ppm
2	25	16
3	25	64
4	25	160
5	25	250
6	25	400

While the breakthrough occurred slightly earlier, the total UDMH picked up was 1.7 meq. Regeneration with 50 ml of N/4 HCl in methanol removed 1.7 meq of UDMH.

A sample of anhydrous hydrazine was obtained at this time and a new feed solution was made up containing equal parts by weight of hydrazine and UDMH. This feed solution behaved identically with the previous UDMH-methanol solution in the column experiments. A series of runs were made in an attempt to optimize the regeneration conditions using methanolic HCl. Acid concentration was varied from 2 N to N/8, amount of acid from 10 to 20 meq, and contact time from 10 to 40 minutes. The results were erratic, partially as a result of analytical difficulties, and possibly partially because of kinetic problems in the non-aqueous system. Certainly more work would be required before the best conditions for such a non-aqueous regeneration scheme could be set.

The original intent in using an all methanol cycle was to avoid contaminating the solvent with water with the subsequent necessity for a drying step. Such a scheme would be attractive if the process were to be run on a frequent cyclic basis. However, in the current use, where the system is to be used only intermittently, rough economic estimates indicate that a disposable resin bed, or even discarding of the methanol might be more attractive overall.

c. UDMH from Freon<sup>®</sup> 113 Using Molecular Sieves

Batch equilibrium studies were carried out to determine equilibrium adsorption of UDMH at various UDMH concentrations. The results, shown in Figure 1a-2, show that UDMH is not strongly adsorbed by molecular sieves containing about 9% water. A column experiment in which Freon<sup>®</sup> 113 containing 500 ppm UDMH was passed through a column of molecular sieves containing about 9% water, gave similar results, namely poor adsorption of UDMH.

d. UDMH from Freon<sup>®</sup> 113 Using Silica Gel

Batch equilibration of 500 ppm UDMH solution in Freon<sup>®</sup> 113 with silica gel containing about 9% water showed rather strong adsorption of UDMH. These results are shown in Figure 1a-3. A column experiment, using a 2 ml measuring pipet containing 2.0 ml silica gel (9% water content) as the column, gave evidence of good adsorption of UDMH, although air pockets in the column caused operating problems. Another column run,

using 3.4 ml of silica gel in a column 3/8" x 8", showed good pickup of UDMH with little leakage of UDMH. The results of this run are shown in Figure 1a-4, where it can be seen that 73 bed volumes can be treated to a 5 ppm UDMH breakthrough, or 88 bed volumes to a 10 ppm UDMH breakthrough. When word was received that methanol would probably be used as the solvent for the fuels, work on this type adsorbent was discontinued, since the use of adsorbents containing water require an immiscible solution for application.

#### 4. Oxidizer Side

##### a. N<sub>2</sub>O<sub>4</sub> from Freon<sup>®</sup> 113 by Ion Exchange

A column containing 1 ml of Dowex<sup>®</sup> 21K, Cl<sup>-</sup>, was regenerated with 10.0 ml of N NaOH. The Cl<sup>-</sup> eluted was 1.05 meq. The excess water was blown out of the column and a 380 ppm (0.013 N) solution of N<sub>2</sub>O<sub>4</sub> in Freon<sup>®</sup> 113 was passed through it. The flow rate varied from 0.5 to 2.0 ml/minute. The acid in the effluent averaged about 3 ppm (expressed as N<sub>2</sub>O<sub>4</sub>) for the first 275 ml collected. This represents an acid pickup of over 3.5 meq on a column with an exchange capacity of 1.05 meq. There was no breakthrough to feed concentration at this point. Instead, the effluent concentration rose to about 45 ppm and held there for another 300 ml of effluent at which point the run was stopped. This represents the pickup of approximately another 3.5 meq of acid. At this point the column was regenerated with 25.0 ml of N NaOH and the regenerant effluent and rinse-back titrated with standardized HCl. This titration indicated that 5.8 meq of anion was stripped from the column, which substantiates the 7.0 meq picked up.

The water swollen Dowex<sup>®</sup> 21K obviously has a considerable sorptive capacity for N<sub>2</sub>O<sub>4</sub> in this system, enough so that it would appear potentially hazardous in that the organic resin might easily accumulate enough N<sub>2</sub>O<sub>4</sub> to trigger a violent oxidation. There was a chemical reaction in the resin as shown by a slow continuous generation of gas in the column. This gas evolution appeared to continue even after the regeneration with NaOH. Attempts to detonate a few beads of the loaded resin with a hammer failed. When ignited in a flame they did not show any tendency to sputter or pop.

Removal of N<sub>2</sub>O<sub>4</sub> from Freon<sup>®</sup> 113 was also tried using Dowex<sup>®</sup> 44, an ammonia-epichlorohydrin condensation resin. The resin was converted to the free-base form and

thoroughly rinsed. One ml of the resin was placed in the column and a 500 ppm  $N_2O_4$  in Freon<sup>®</sup> 113 was passed through it. A volume of 125 ml was collected with a residual acid of about 5 ppm  $N_2O_4$ . By the end of this volume the flow had practically stopped because of increased pressure drop in the bed. After standing overnight, the upper portion of bed was found to be softened and even partially liquified.

b.  $N_2O_4$  from Freon<sup>®</sup> 113 by Degassing

In working with the  $N_2O_4$ -Freon<sup>®</sup> 113 solutions, it was observed that  $N_2O_4$  was lost from solution at an appreciable rate if the container was left open to the atmosphere. It therefore seemed logical to try a degassing or desorption scheme.

A small desorption unit was set up as in Figure 1a-5. The size of the packed column was roughly 8" x 1" and the packing was 1/4" saddles. The liquid distribution was quite poor and it tended to run down the sides of the column. The sweep gas was plant nitrogen; the flow rate was measured by means of a small rotameter, and controlled at roughly 5 ml/second. The exit gas was bubbled through a solution of standardized caustic.

In the first run the feed solution contained 712 ppm of  $N_2O_4$ . Two 100 ml cuts were obtained:

<u>Cut No.</u>	<u>Ave. Flow Rate</u>	<u>Residual Acid</u>	<u>As <math>N_2O_4</math></u>
1	1.65 ml/minute	0.00148 <u>N</u>	43 ppm
2	2.2 ml/minute	0.00137 <u>N</u>	40 ppm

There was no color left in the product. The amount of caustic neutralized in the scrubber was 4.5 meq. The approximate amount of acid removed from the product =

$$V\Delta C = 200 \text{ ml } (0.0244 \text{ N } - 0.0014 \text{ N}) = 4.6 \text{ meq}$$

In a second more extended run air was used as the sweep gas and the feed contained 506 ppm  $N_2O_4$ . A total of 4,314 g of product (I) was collected at an average flow rate of 1.2 g/minute ( $\sim 0.8$  ml/minute). This had a residual content of 0.0021 N (61 ppm as  $N_2O_4$ ). In a third run using the same feed but at an average flow rate of 13.2 g/minute (8.4 ml/minute), 1,320 g of product (II) was obtained with a residual acid content of 0.0043 N (125 ppm as  $N_2O_4$ ). This product had a trace of the brownish  $N_2O_4$  color left in it. There was no appreciable amount of Freon<sup>®</sup> 113 collected in the gas scrubber in any of the runs.

Several techniques were tried for the reduction of the residual acidity from the degassed product. A portion of product (I) was passed through a 1 ml column of Dowex® 21K which had been regenerated with 5.0 ml of N NaOH. ( $\text{Cl}^-$  eluted = 0.84). A total of 1,100 ml was put through the bed and the effluent concentration was still less than  $1 \times 10^{-4}$  N. Total acid picked up was approximately 2.2 meq on an exchange capacity of 0.84 meq. Rinsing the bed with about 70 ml of acetone at this point eluted considerable yellow color and 0.93 meq of acid. There was no noticeable degradation of the resin.

A 200 ml sample of product (I) was allowed to evaporate in a tared dish. The residue was 0.10 g or about 0.03%.

Another portion of product (I) was flash distilled until 98-99% of the material had gone overhead. The residue was found to contain only a trace of acid while the distillate was 0.0015 N, as compared with 0.0019 N before distillation.

A 250 ml portion of product (II) was shaken with 25 ml of water and separated. The Freon® phase was found to have an acid content of only  $9 \times 10^{-5}$  N after this extraction.

As a final step these samples were examined by means of their visible and UV adsorption spectra using a Cary Recording Spectrophotometer. The results are shown in Table Ia-I. The strong peak at  $340\mu$  is the major contribution of the  $\text{N}_2\text{O}_4$ . The absence of any adsorption at this wavelength in product (I) indicates that  $\text{N}_2\text{O}_4$  can be removed completely by careful degassing and that the residual acid is not  $\text{N}_2\text{O}_4$ . The distillation experiment shows that the residual acid base volatility approached that of Freon® 113. The extreme slowness with which it titrates, probably due to a slow diffusion from the organic into the aqueous phase, suggests a rather hydrophobic material. This might be a halogenated organic acid formed from the action of the  $\text{N}_2\text{O}_4$  on some impurity in the Freon® 113. It is not present in the original Freon® 113.

Another unknown impurity which shows an adsorption at  $275\mu$  is a higher boiler than Freon® 113 and may represent an impurity in the  $\text{N}_2\text{O}_4$ , a reaction product of  $\text{N}_2\text{O}_4$  and Freon® 113, or simply some material such as stopcock grease picked up in processing the sample.

c.  $\text{N}_2\text{O}_4$  from Freon® 113 Using Molecular Sieves

Freon® 113 containing about 500 ppm  $\text{N}_2\text{O}_4$  was passed through an 8" high bed of molecular sieves containing

10.6% water. The pickup of  $N_2O_4$  was very poor, the first effluent cut being about 55% of the feed concentration, with subsequent cuts being of even higher concentrations. Next, some molecular sieves were saturated with water prior to loading in an 8" high column. This increased waste content of the molecular sieves resulted in much stronger adsorption of  $N_2O_4$ . While the leakage level was not as low as desired, approximately 175 bed volumes were treated to yield an overall  $N_2O_4$  concentration of 10 ppm.

A problem of molecular sieve degradation appeared during this run. The sieves at the top of the column were reduced to a powder and the sieves were observed to be quite friable when the column was unloaded. In addition, the effluent during the water regeneration, produced a white flocculent precipitate when it was titrated to a neutral pH. X-ray diffraction of the ignited precipitate indicated that it was  $Al_2O_3$ , thus confirming the belief that the flocculent precipitate was  $Al(OH)_3$ . Thus, molecular sieves do not appear to have sufficient chemical stability for this application.

The use of a bed of dry molecular sieves as an adsorbent for  $N_2O_4$  from Freon<sup>®</sup> 113 was also investigated. In this case, the molecular sieves would act as an adsorbent of polar molecules rather than as a support for water. This system was found to be ineffective however, the first effluent cut containing 12 ppm  $N_2O_4$ , the next cut containing 55 ppm  $N_2O_4$ .

d.  $N_2O_4$  from Freon<sup>®</sup> 113 Using Silica Gel

Two series of equilibration experiments were carried out using silica gel containing about 9% and about 16.7% water. In both cases, the adsorption was not very strong at low concentrations of  $N_2O_4$ , although strong adsorption was observed at higher concentrations. The adsorbent with the higher water content showed the stronger adsorption of  $N_2O_4$ , as can be seen from Figure 1a-6, which shows the results for both adsorbents.

In a column contact of 500 ppm  $N_2O_4$  solution with silica gel containing about 9% water, the effluent showed a gradual increase in  $N_2O_4$  concentration; only the first fraction was at a  $N_2O_4$  level below 10 ppm. The next column experiment, with silica gel containing 21.9% water, gave lower  $N_2O_4$  levels in the effluent than in the previous run, but again showed a steady increase in  $N_2O_4$  leakage from the start of the run. Again, only the final fraction contained less than 10 ppm  $N_2O_4$ . The elution of the adsorbed  $N_2O_4$  with

water showed complete removal, with most of the desorbed material coming off in the first fraction.

In an attempt to increase the adsorption of the  $N_2O_4$ , a quantity of silica gel was equilibrated with 1  $N$  NaOH solution. After removal of the gel from the NaOH solution, it was placed in an 8" high column and rinsed with Freon<sup>®</sup> 113, prior to passage of Freon<sup>®</sup> 113 containing about 500 ppm  $N_2O_4$  through the column. This adsorbent was found to give much lower  $N_2O_4$  levels in the effluent. Approximately 140 bed volumes of effluent were treated to a breakthrough of 5 ppm  $N_2O_4$ . Removal of the adsorbed material was attempted by eluting the bed with water. The first fraction was acidic, and titration of this acid accounted for 63% of the  $N_2O_4$  adsorbed. Subsequent fractions were alkaline, due to the NaOH leaking from the bed. It should be noted that the adsorbent held material in excess of that neutralized by the NaOH trapped in the gel.

In order to determine whether any of the NaOH in the silica gel might diffuse into the Freon<sup>®</sup> solution as it passes through the column, an experiment using radioactive sodium was run. The 1  $N$  NaOH solution was spiked with  $Na^{22}$  prior to equilibration of the solution with the silica gel. The gel was then dried on a paper towel to remove excess solution. The radioactivity of the gel was determined and compared to the radioactivity of the solution before contact with the gel. The activity on the gel was 71.5%. The gel was then placed in an 8" high column and rinsed with Freon<sup>®</sup> 113. No activity was detected in this Freon<sup>®</sup> 113. Next, a 500 ppm solution of  $N_2O_4$  in Freon<sup>®</sup> 113 was passed through the column and fractions collected. In order to concentrate the  $Na^{22}$  activity, each 100 ml fraction was shaken with 2.0 ml of a hydrogen form cation exchange resin (Dowex<sup>®</sup> 50W-X4, 50-100 mesh). After contact, the resin was filtered, rinsed with water, and transferred to a test tube for counting. The results are given in Table Ia-II, which gives the activity of the samples, the  $Na^+$  concentration calculated from the activity, and the concentration of  $N_2O_4$  or hydrolysis products in the fractions. The erratic behavior observed is unexplained, although the amount of  $Na^+$  leaked out by the Freon<sup>®</sup> 113 is certainly below maximum allowable limits.

Water elution was used to desorb the  $N_2O_4$  and hydrolysis products. Most of the  $Na^{22}$  activity eluted in the first fraction. The gel was counted after water elution and found to contain no  $Na^{22}$  activity. A material balance

on the  $\text{Na}^{22}$  activity was not obtained because of the resin contact method for concentrating the activity. In the effluent samples during the water elution, the high acid concentration prevented complete pickup of the  $\text{Na}^+$  ions on the resin.

To investigate the effect of a higher flow rate on the pickup of  $\text{N}_2\text{O}_4$  by silica gel containing  $\text{NaOH}$ , a run was made at a higher flow rate. The silica gel was equilibrated as before with 1 N  $\text{NaOH}$ . The column was ~17" high and 0.342" in diameter. The flow rate averaged 11.1 ml/minute, which is equivalent to 4.6 gallons/sq.ft./minute. At this high flow rate, it was visually noted that the leading edge of the adsorption band was fairly broad, approximately 6" in width. The results of this run are shown in Figure 1a-7, where it can be seen that the lowest concentration of  $\text{N}_2\text{O}_4$  in the effluent was 7 ppm.

e.  $\text{N}_2\text{O}_4$  Extraction from Freon<sup>®</sup> 113 with Water

In order to study the feasibility of extraction of  $\text{N}_2\text{O}_4$  from Freon<sup>®</sup> 113 with water, the partition of  $\text{N}_2\text{O}_4$  between these two phases was studied. (This was accomplished by shaking water with a solution of  $\text{N}_2\text{O}_4$  in Freon<sup>®</sup> 113 until equilibrium was obtained, followed by an analysis of  $\text{N}_2\text{O}_4$  concentration in each phase. Various points on the curve were generated by varying the ratio of the two phases.) The results are shown in Figure 1a-8. It can be seen that the  $\text{N}_2\text{O}_4$  concentration in the water phase is directly proportional to its concentration in the Freon<sup>®</sup> 113 phase with a distribution coefficient of 157, i.e. the  $\text{N}_2\text{O}_4$  concentration in water divided by the  $\text{N}_2\text{O}_4$  concentration in Freon<sup>®</sup> 113. The rate of extraction of  $\text{N}_2\text{O}_4$  from Freon<sup>®</sup> 113 was studied by shaking a 500 ppm  $\text{N}_2\text{O}_4$  solution in Freon<sup>®</sup> 113 with water at a phase ratio of 10:1 (organic:aqueous), followed by analysis of the  $\text{N}_2\text{O}_4$  concentration in each phase. The results are shown in Figure 1a-9, where it can be seen that extraction is virtually complete after 5 minutes.

C. Conclusions

Hydrazine-UDMH from Methanol

Cation exchange resin removal is recommended.

Resin: Dowex<sup>®</sup> 50W-X8, 50-100 mesh,  $\text{H}^+$ .

Operation: One cycle; no regeneration.



Capacity: 1075 gal. 500 ppm feed/cu.ft.

Flow Rate: 3 gpm/ft.<sup>2</sup>

Bed Depth: 3-5 ft.; diameter as needed.

Pre-Rinse: 5 bed volumes methanol.

Column Design: Standard, fixed bed.

Breakthrough: Analysis by pH.

N<sub>2</sub>O<sub>4</sub> from Freon<sup>®</sup> 113

Choice to be made between (1) caustic in silica gel, (2) water extraction, or (3) degassing or combination of (3) with (1) or (2).

D. TablesTABLE 1a-ISpectral Properties of Degassed Samples

<u>Sample</u>	<u>Residual Acid (At N<sub>2</sub>O<sub>4</sub>)</u>	<u>Spectral Characteristics</u>	<u>Adsorption at 340 <math>\mu</math></u>	<u>275 <math>\mu</math></u>
Freon 113	---	No adsorption above 250 $\mu$ , opaque below 230 $\mu$	0	0
500 ppm N <sub>2</sub> O <sub>4</sub> in Freon 113	500	Increasing adsorption from 600 $\mu$ to 380 $\mu$ , strong peak at 340 $\mu$ , opaque below 290 $\mu$	1.59	?
Degassed, Product I	61	No adsorption above 300 $\mu$ , distinct peak at 275 $\mu$	0	0.86
Degassed, Product II	125	Small peak at 340 $\mu$ , sharp peak at 275 $\mu$	0.11	1.07
Product I + Ion Exchange	<1	Unchanged from Product I	0	0.87
Product I + H <sub>2</sub> O Extraction	2.6	Unchanged from Product I	0	0.99
Product II + Distillation	43.5	No absorption above 300 $\mu$ , small adsorption 280-250 $\mu$	0	0.03

TABLE 1a-II

Na<sup>22</sup> LEAKAGE FROM NaOH TREATED SILICA GEL

<u>Fraction<sup>(1)</sup></u>	<u>N<sub>2</sub>O<sub>4</sub> Concentration</u>	<u>Na<sup>22</sup> Activity<sup>(2)</sup></u>	<u>Na Concentration</u>
1	-	496 counts/min. (510)	Nil
2	.00037 <u>N</u> 10.8 ppm		
3	.00018 <u>N</u> 5.3 ppm		
4	.00004 <u>N</u> 1.2 ppm	901 (510)	6.6 x 10 <sup>-6</sup> <u>N</u> .084 ppm
5	-	614 (510)	1.8 x 10 <sup>-6</sup> <u>N</u> .025 ppm
6	.00006 <u>N</u> 1.8 ppm	440 (425)	2.5 x 10 <sup>-7</sup> <u>N</u> .0035 ppm
7	.00037 10.8 ppm	524 (425)	1.7 x 10 <sup>-6</sup> <u>N</u> .024 ppm

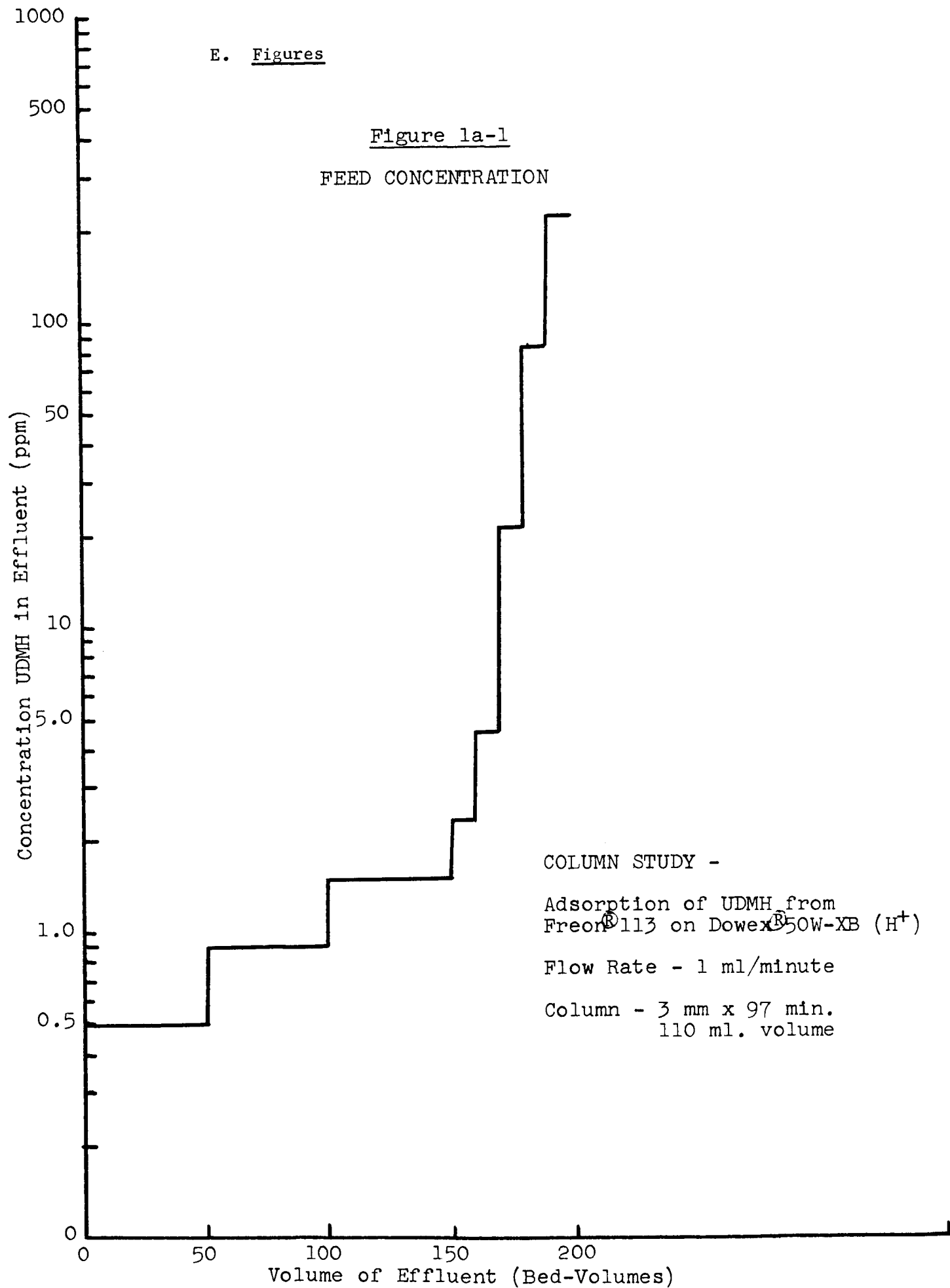
(1) All fractions 100 ml volume.

(2) Figures in parentheses are background counts.

E. Figures

Figure 1a-1

FEED CONCENTRATION



COLUMN STUDY -

Adsorption of UDMH from  
Freon® 113 on Dowex® 50W-XB ( $H^+$ )

Flow Rate - 1 ml/minute

Column - 3 mm x 97 min.  
110 ml. volume

Figure 1a-2

EQUILIBRATION STUDY

Removal of UDMH From Freon<sup>®</sup> 113  
by Molecular Sieves 5H (9% H<sub>2</sub>O)

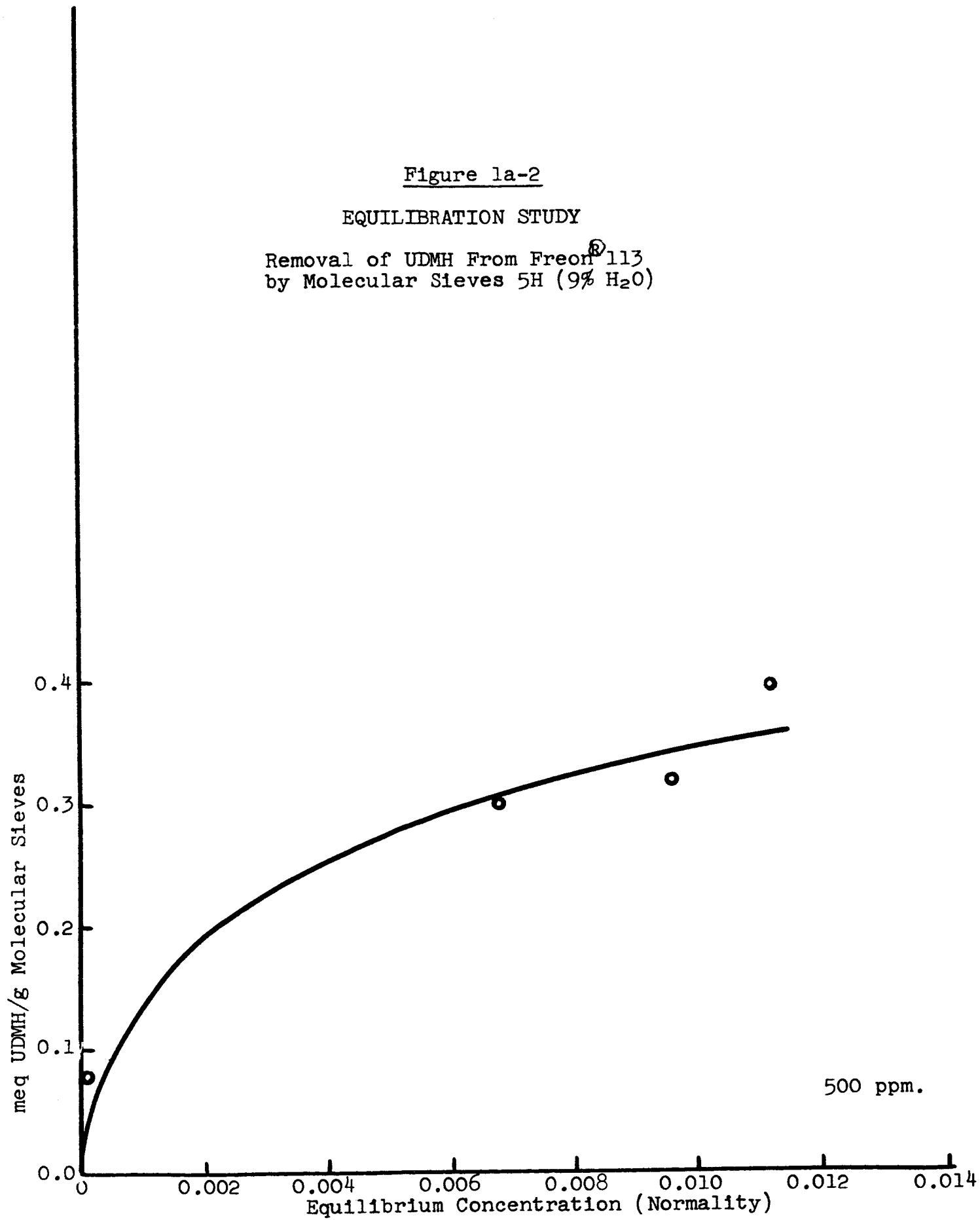


Figure 1a-3

REMOVAL OF UDMH FROM FREON<sup>®</sup> 113 BY  
SILICA GEL (9% H<sub>2</sub>O)

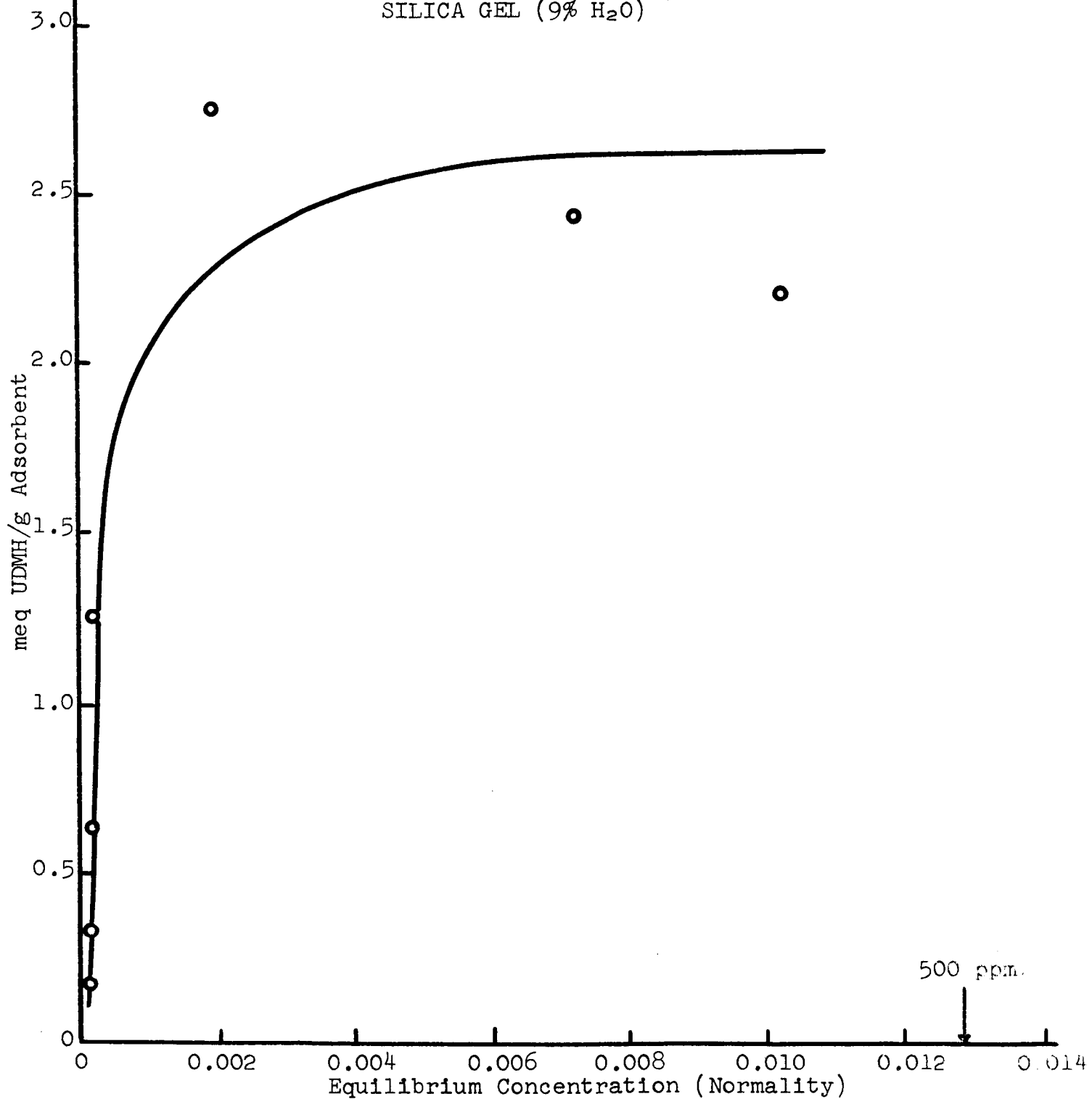


Figure 1a-4

COLUMN STUDY

REMOVAL OF 500 PPM UDMH IN FREON<sup>®</sup> 113  
SILICA GEL COLUMN  
(3.4 ml, 2.915 g)

9% H<sub>2</sub>O in Silica Gel

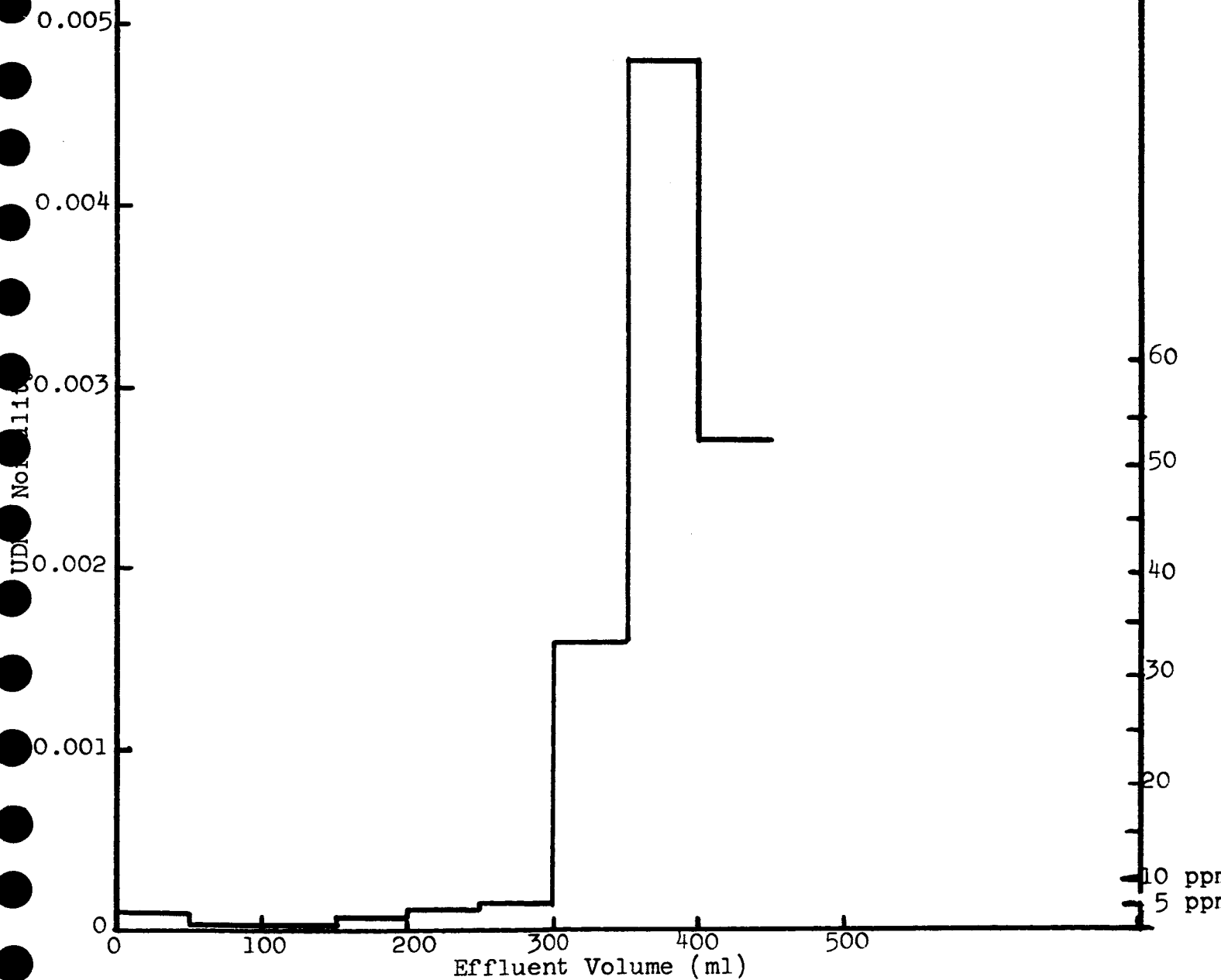


Figure 1a-5

Extraction Apparatus

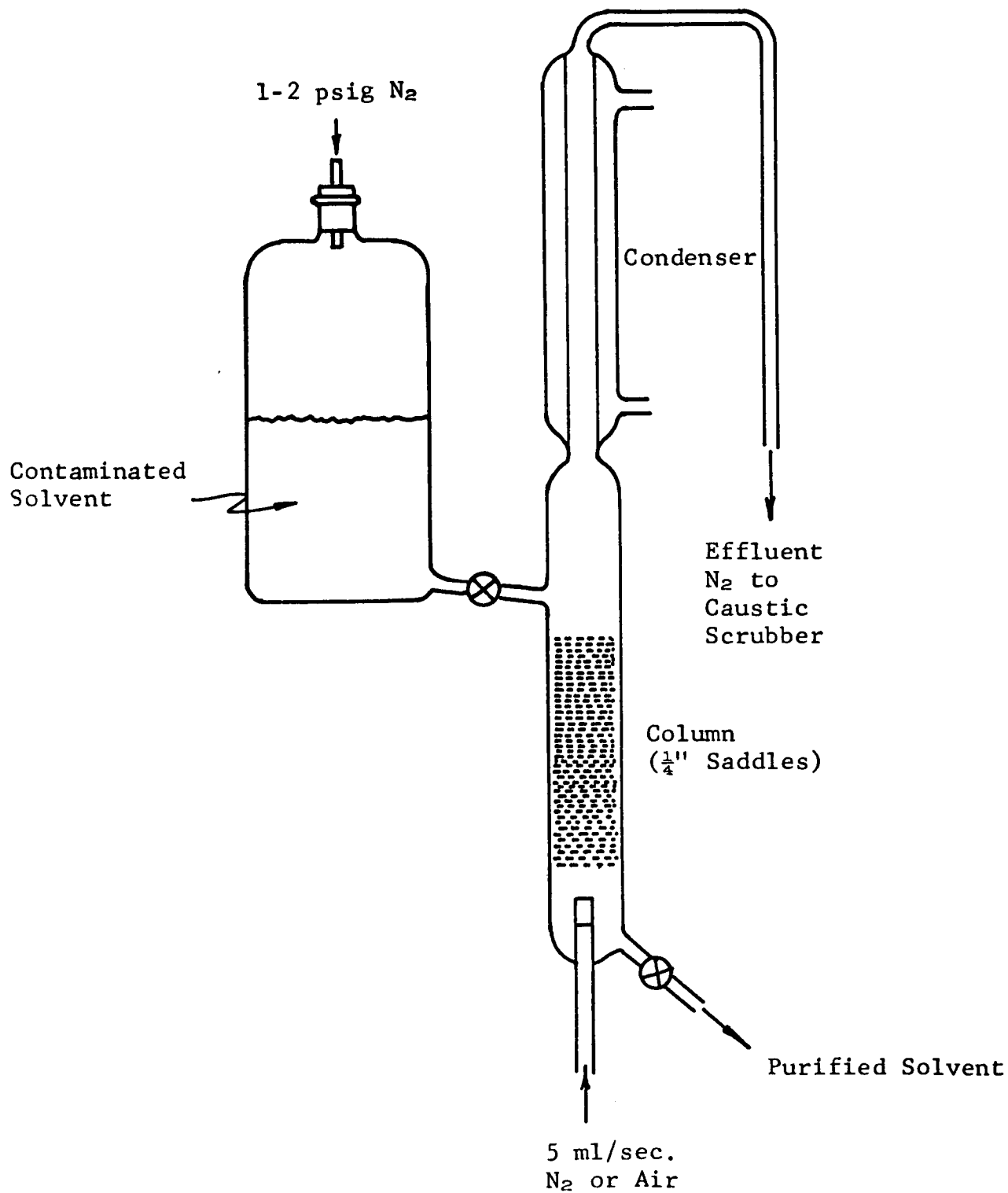




Figure 1a-6

EQUILIBRATION STUDY  
REMOVAL OF  $\text{N}_2\text{O}_4$  FROM FREON<sup>®</sup> 113 (~500 PPM)  
WITH SILICA GEL

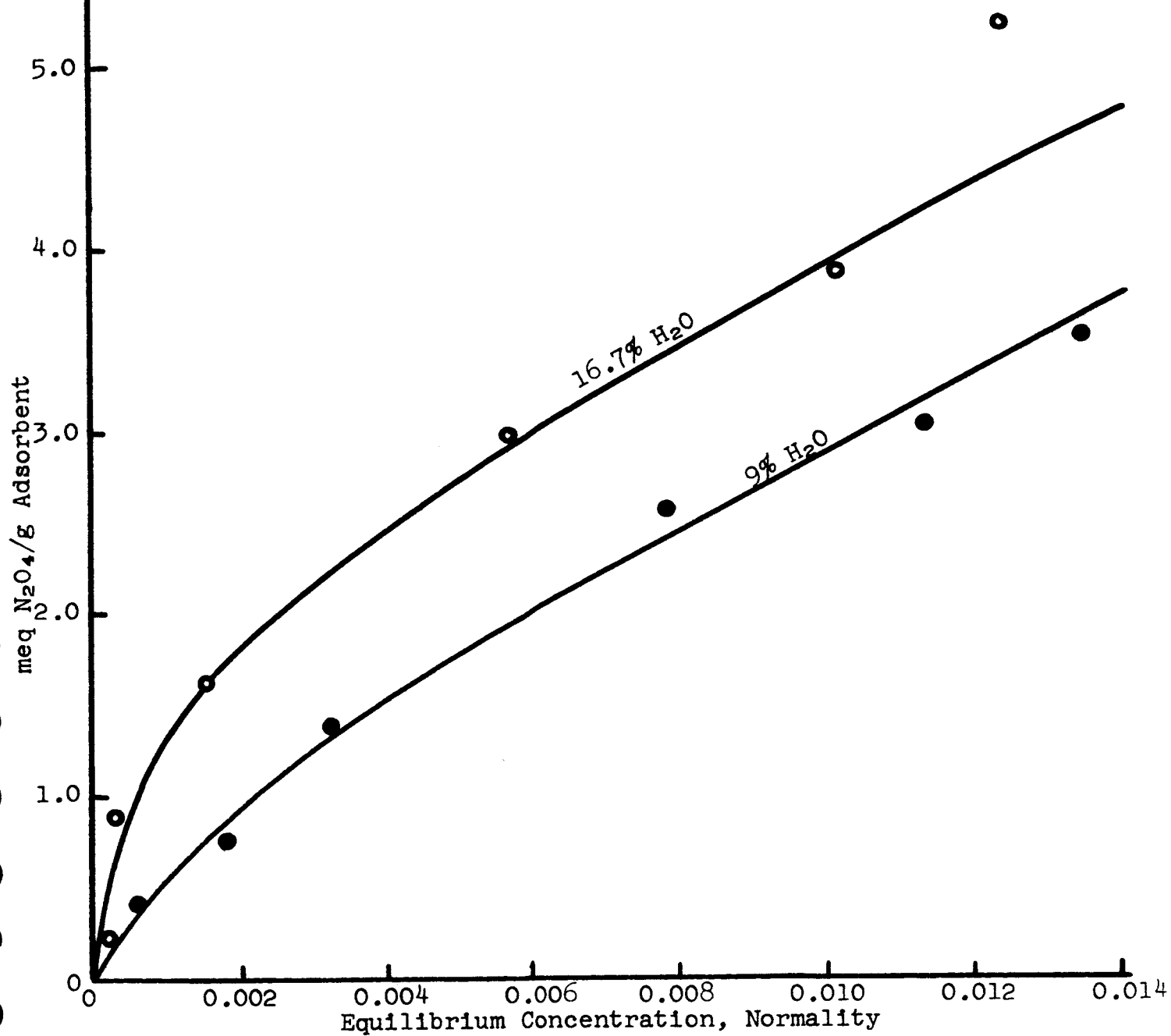


Figure 1a-7

COLUMN STUDY  
ADSORPTION OF  $N_2O_4$  FROM FREON<sup>®</sup> 113  
WITH SILICA GEL (NaOH TREATED)  
AT HIGH FLOW RATE

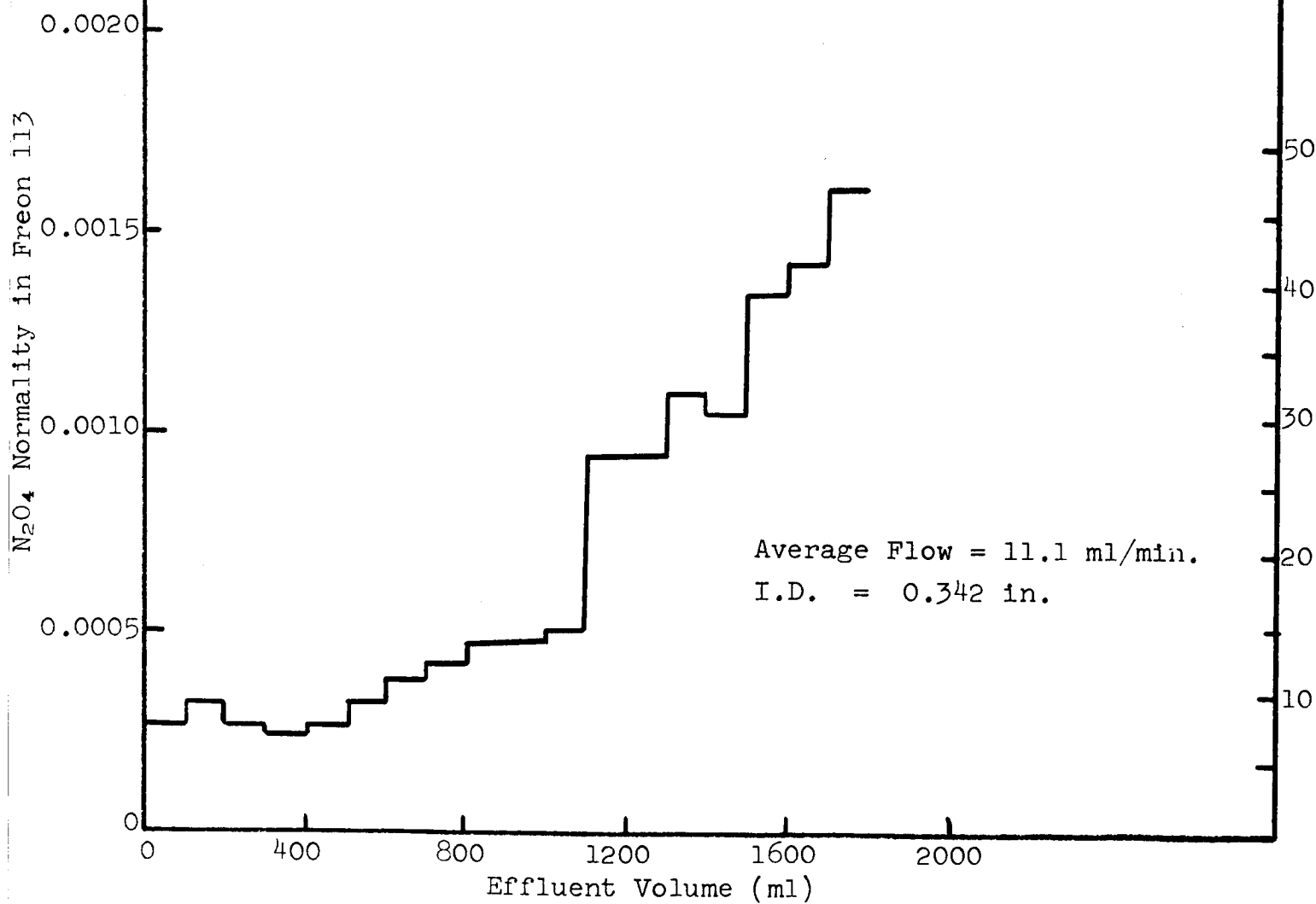


Figure 1a-8

DISTRIBUTION OF  $N_2O_4$   
BETWEEN  $H_2O$  AND FREON<sup>®</sup> 113

$N_2O_4$  Normality in Water Layer

0

0.3

0.2

0.1

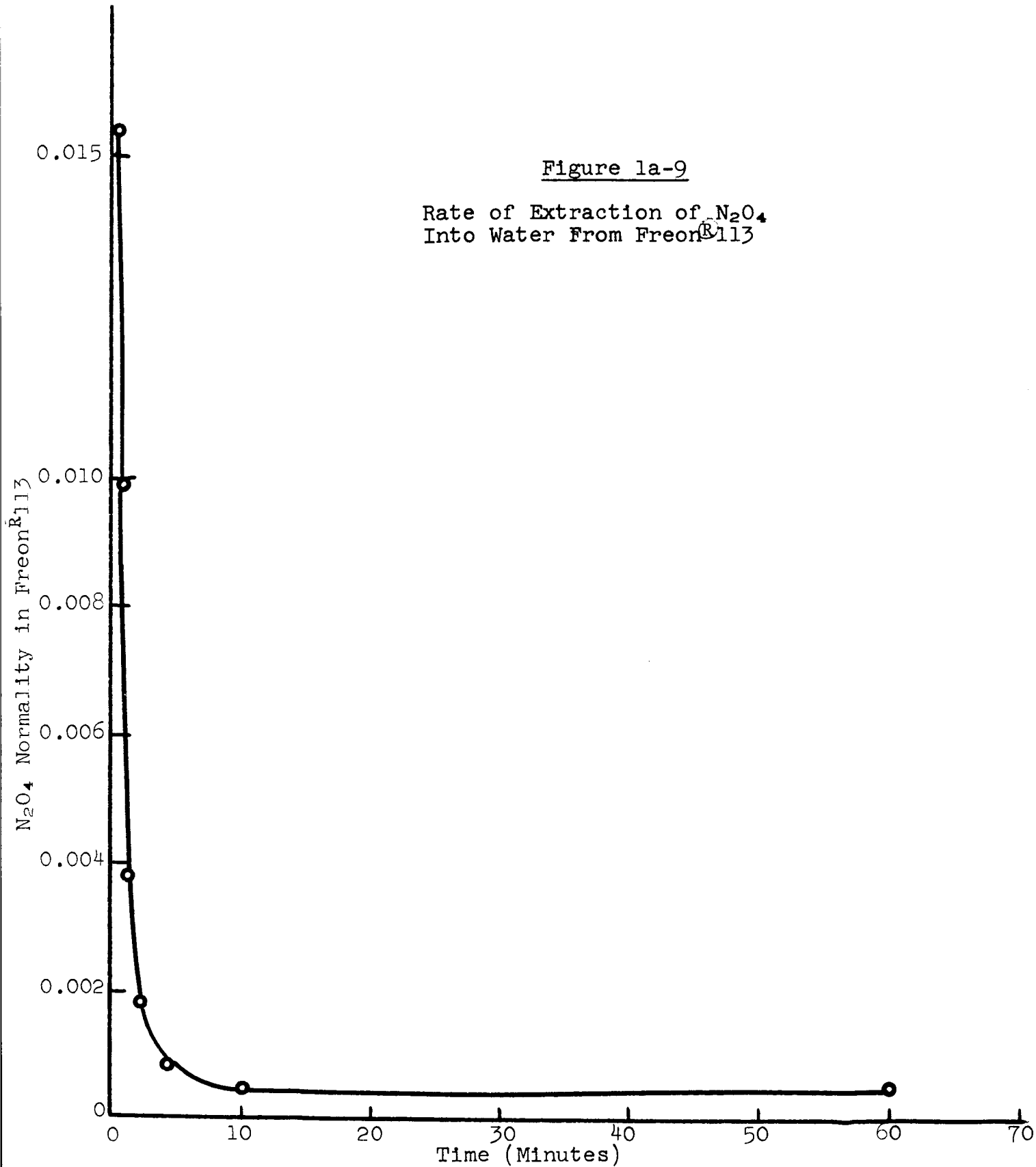
$$K_d = \frac{[N_2O_4 (H_2O)]}{[N_2O_4 (Freon^{®} 113)]} = 157$$

0.001

0.002

$N_2O_4$  Normality in Freon Layer

Figure 1a-9  
Rate of Extraction of  $\text{N}_2\text{O}_4$   
Into Water From Freon<sup>®</sup> 113



## VIII. UNIT 2 - SOLVENT DEVELOPMENT

### A. Summary

1. Correlating the results of the thermodynamic calculations with the knowledge of compatibility gained from the detonation tests, the following generalizations appear valid:
  - a. Solvent-N<sub>2</sub>O<sub>4</sub> systems having a  $\Delta F$  value less than 2 Kcal/gram N<sub>2</sub>O<sub>4</sub> are not detonatable regardless of the size of the triggering charge. These solvents are compatible with N<sub>2</sub>O<sub>4</sub>.
  - b. Solvent-N<sub>2</sub>O<sub>4</sub> systems showing a  $\Delta F$  value greater than 2 Kcal/gram N<sub>2</sub>O<sub>4</sub> can be detonated if given sufficient shock. These solvents are not compatible with N<sub>2</sub>O<sub>4</sub>.
2. The results of the compatibility study of elastomers with candidate solvents are given below:
  - a. Teflon<sup>®</sup> TFE and FEP are compatible with the propellant and all solvents.
  - b. Kel-F No. 300 was not compatible with the propellant. Failure occurred within one week in the N<sub>2</sub>O<sub>4</sub> test and within three weeks in the Aerozine-50 test.
  - c. Kynar was found to be compatible with propellant and solvents.
  - d. Stillman SR634-70 rubber was not compatible with Aerozine-50. Failure occurred within five weeks. By comparison, B. F. Goodrich' IIR-50 butyl rubber showed a gain in tensile strength.
  - e. Rulon was found to be compatible with propellant and solvents.
3. The elastomers absorb a substantial quantity of propellant. The results show that the amount of contaminant diffused from the elastomer per unit of time is proportional to the amount present at that time; therefore, the rate the contaminant diffuses from the elastomer can be expressed mathematically by this equation:

$$K = \frac{2.303}{t_2 - t_1} \cdot \log \frac{c_1}{c_2}$$

where:  $c_1$  = the initial concentration  
 $c_2$  = the final concentration of contaminant  
          in the elastomer  
 $t_1$  = the initial time  
 $t_2$  = the final time

The constant (K) is the specific rate constant or velocity constant for a first order reaction.

- a. The specific rate (K) for the diffusion of  $N_2O_4$  from Teflon® FEP at ambient temperature shows values of  $1.4 \times 10^{-3}$ ,  $1.5 \times 10^{-3}$ , and  $1.8 \times 10^{-3}$  in environments of  $GN_2$ , Freon® TF, and  $CCl_4$ . These results show the diffusion rate to be independent of environment.
  - b. The diffusion of A-50 from Stillman rubber at ambient conditions in environments of  $GN_2$  and methanol shows a (K) value of  $3.06 \times 10^{-4}$  for both environments.
  - c. The results of  $N_2O_4$  diffusion from Teflon® FEP tests made at  $25^\circ$ ,  $65^\circ$ , and  $100^\circ$  C using  $GN_2$  purge show (K) values of  $1.4 \times 10^{-3}$ ,  $3.4 \times 10^{-3}$ , and  $1.1 \times 10^{-2}$ . This implies that the diffusion rate is temperature dependent. Plotting these points on semilog paper shows a reasonable fit; therefore, the diffusion rate increases exponentially as the temperature is increased.
4. The results of tests show that the flushing solvents can tolerate several hundred parts per million of the contaminants and still effectively extract the contaminant from the elastomer.

## B. Solvent Selection

### 1. Candidate Solvent Listing

A list of candidate solvents (over 200) was compiled. No consideration was given in this compilation to availability or cost. This master list was reviewed and solvents were selected as promising candidates. These solvents are shown in Table 2-I. Each of these solvents was subjected to at least one test of some type.

### 2. Thermodynamic Calculations

Some thermodynamic calculations for the reactions of nitrogen tetroxide with various solvents were made to determine if a correlation could be drawn between the energy change and compatibility. The heat of reaction  $\Delta H_{300^\circ K}$  and the change in free energy  $\Delta F_{300^\circ K}$  were determined according to the following equations:

$$\Delta H = (H_F N_2O_4 + H_F \text{ Solvent}) - (H_F \text{ Products})$$

$$\Delta F = (F_{N_2O_4} + F_{\text{Solvent}}) - (F_{\text{Products}})$$

The results are given in Table 2-II, which lists the assumed or possible reaction of solvent and oxidizer together with the calculated heat of reaction and free energy change.

In considering the equilibria involved in the assumed reaction, the further assumption was made that the reaction would ultimately go to completion, bearing in mind the possibility of stepwise and side reactions. The heat of reaction and free energy changes in each case were negative indicating heat would be evolved and the reaction would proceed.

Correlating the results of these calculations with the knowledge of compatibility gained from the empirical detonation tests, the following generalizations would appear valid: (1) Solvent- $\text{N}_2\text{O}_4$  systems showing a  $\Delta F$  value less than 2 Kcal/gram  $\text{N}_2\text{O}_4$  are not likely to be detonated regardless of the size of the triggering charge. (2) Solvent- $\text{N}_2\text{O}_4$  systems showing a  $\Delta F$  value greater than 2 Kcal/gram  $\text{N}_2\text{O}_4$  can probably be detonated given sufficient shock.

These considerations point out that compatibility of solvents with  $\text{N}_2\text{O}_4$  covers a broad spectrum of values relating to the initiating charge required for detonation. There are presently no standard requirements or standardized testing procedures.

All results which are currently available are based upon arbitrary conditions of charge, placement of charge, and concentration.

### 3. Compatibility Tests

Compatibility tests were made to determine the effect of propellant and various solvents on the soft parts. The test procedure used was ASTM Designation D543-60T, "Resistance of Plastics to Chemical Reagents." This method includes procedures for measuring changes in weight, dimensions, appearance and strength properties. The materials used in this study are the elastomers and solvents shown in Table 2-III. The results are also given in this table. The elastomer was considered not compatible with the solvent if the elastomer showed a loss of 25% in tensile strength.

### C. Fundamental Study of Degassing of the Contaminants From Elastomers

The elastomers contain the residual-propellant contaminants that remain after the Apollo tanks have been flushed with a solvent. Previous work indicated that the contaminants are absorbed in the capillaries of the elastomers and, consequently, the source of contamination. Therefore, a study was initiated to determine the rate at which the contaminants degassed from the elastomers.

## 1. Procedure

The procedure used in carrying out these tests at ambient conditions is as follows. Sample specimens of the elastomer were immersed in the contaminant ( $N_2O_4$  or A-50) for several days, and the weight gain was recorded. After determining the contaminant content of each specimen, they were placed individually in 50 milliliters of the solvent under test. The samples were removed from the solvent at specified time intervals and weighed, and the contaminant content of the solvent was determined.

The tests made at elevated temperatures were carried out in this manner. The solvent was placed in a round-bottomed flask which was provided with a heating mantle. Heat was applied, and the temperature of the solvent was increased to boiling. The vapors from the boiling solvent were introduced into the top of a metal test chamber. Specimens of the elastomer containing the contaminant were positioned in the chamber between wire screens. The rate at which the solvent was boiled off was sufficient to maintain vapors in the chamber after the chamber reached the boiling temperature of the solvent. The exit vapors passed through a condenser and the condensate collected in a graduate. The amount collected in a specified time interval was noted, and the contaminant in the condensate determined. The test using steam was essentially carried out in the same manner as the solvent test except that the steam was received from a low pressure steam line. Approximately 13 psig steam pressure was maintained by snubbing the valve in the line of the test chamber. Other test procedures used will be described when the specific test is discussed.

## 2. Degassing of $N_2O_4$ From the Elastomers

The first objective was the screening of selected solvents to determine if one was more effective than the others in the removal of  $N_2O_4$  from the elastomers. The solvents used were Freon<sup>®</sup> MF, Freon<sup>®</sup> TF, carbon tetrachloride, and  $GN_2$ . The elastomers used were Teflon<sup>®</sup> FEP, Teflon<sup>®</sup> TFE, Rulon, and Kynar. The procedure, described above, was used in carrying out the tests. The results are given in Tables 2-IV through 2-IX. These tables show the elastomer, solvent, the time in minutes that the elastomer was immersed in the solvent, the  $N_2O_4$  absorbed in the elastomer expressed in milligrams per square centimeter, and the percent of  $N_2O_4$  retained in the elastomer.

The results show, at ambient temperature, that all of the solvents and  $GN_2$  have about the same  $N_2O_4$  removal rate. An increase in the temperature shows a definite increase



in the amount of  $N_2O_4$  removed in a given period of time. Rulon and Kynar absorbed more  $N_2O_4$  than did the Teflons.®

3. Removal of Aerozine-50 From Stillman SR634-70 Rubber

Stillman SR634-70 Rubber was the elastomer of primary concern in the fuel side since the other elastomers did not absorb an appreciable amount of A-50. A series of tests was made to determine the removal rate of A-50 from the Stillman rubber at ambient temperatures using methanol, water, acetone, iso-octane, benzene, and formamide. The procedure was the same as described previously which consisted of immersing the contaminated specimens in solvent for specified time intervals. The results of these tests are given in Tables 2-X and 2-XI. The only significant difference shown by the results was that benzene and iso-octane appear to be superior solvents, but these solvents caused considerable distortion (swelling and elongation) of the specimens. These solvents are not compatible with the rubber.

The rate at which A-50 was removed from Stillman rubber using a gaseous nitrogen purge was investigated at 25° C and 90° C. The apparatus used for the 25° C test consisted of a 200-milliliter, stainless steel test chamber. The specimens were sandwiched between stainless steel wire screens and placed in the chamber. A fixed rate of nitrogen gas was introduced into the top of the chamber, and the exit gas was scrubbed with water to catch the A-50. The water trap was changed at specified time intervals and A-50 determined. A Cenco moisture balance purged with  $GN_2$  was used in carrying out the 90° C test. The balance was equipped with an infrared lamp to supply the heat, and a galvanometer was used to measure the temperature. The weight loss was determined directly from a rotating scale. The results of these tests are given in Table 2-X. The results shown in this table indicate that, after 240 minutes, 93.1 percent of the A-50 was retained at ambient temperature and, after 80 minutes at 90°, only 13.6 percent was retained.

The removal of A-50 from Stillman rubber at 65° C and 100° C was determined using methanol and isobutanol vapors using the procedure described previously. The results are given in Table 2-XIII and are consistent with the previous results in that the A-50 degassing rate is increased at the higher temperature. Table 2-XIV shows the removal of A-50 from the rubber using 13 psig steam (119° C). The results show that approximately 97.5 percent of the A-50 was removed in 168 minutes.

#### D. Discussion of Results

The degassing of the elastomers expressed in milligrams per square centimeter given in Tables 2-IV through 2-XIV is shown graphically in Figures 2-1 through 2-13. The figures show a plot on semi-log paper of the degassing value ( $\text{mg}/\text{cm}^2$ ) versus time.

A straight line was obtained for each test, indicating that the amount of materials degassed from the elastomers per unit of time is proportional to the amount present at that time. The fact that this rate of decrease is proportional to the amount of materials present can be expressed mathematically by the equation:

$$-\frac{dc_A}{dt} = K_{cA} \quad (1)$$

where:  $c$  = the concentration of degassing material (A)  
 $K$  = a proportionality factor  
 $t$  = time  
 $-dc/dt$  = the rate the concentration in the elastomer decreases

Integrating Equation (1) between the limits of concentration ( $c_1$ ), at time ( $t_1$ ), and ( $c_2$ ) at a later time ( $t_2$ ) is shown below:

$$\int_{c_1}^{c_2} \frac{dc}{c} = K \int_{t_1}^{t_2} dt =$$
$$-\ln c_2 - (-\ln c_1) = K(t_2 - t_1)$$
$$K = \frac{2.303}{t_2 - t_1} \cdot \log \frac{c_1}{c_2} \quad (2)$$

This is the equation usually given for a first order reaction.

The constant ( $K$ ) is called the specific rate constant or the velocity constant, and for a first order reaction, it is a number per unit of time. It is evident from Equation (2) that a straight line is produced when the logarithm of the concentration is plotted against time. The rate constant ( $K$ ) can be calculated in Figures 2-1 through 2-13 by multiplying the slope of the line by -2.3 as follows:

$$K = -2.3(\text{slope}) \quad (3)$$

The specific degassing rate constants ( $K$ ) were determined by Equation (3).

Inspection of the figures shows that, in most cases, the degassing of  $N_2O_4$  from the elastomer shows the curves have two slopes which means there is a change in the degassing rate. The break in the curve usually occurred in about two hours, and evaluating (K) shows the degassing rate was considerably reduced after this time. The degassing rate constants (K) are summarized in Tables 2-XV and 2-XVI for  $N_2O_4$  and A-50, respectively.

It was anticipated that the specific degassing rate constant would be an excellent way to compare solvents. The order of magnitude of the specific rate constants was found to be about the same for all solvents and also for  $GN_2$  at the same conditions. This means that the rate that contaminants come out of the elastomers is independent of the environment at room temperature. Since this phenomenon was observed, other variables that might affect the rate constant were considered. The variable that was most obvious was temperature since a slight change (increase) can sometimes double the rate of a reaction. Therefore, one test was made at  $65^\circ C$  to determine if this affected the degassing rate of  $N_2O_4$  from Teflon<sup>®</sup> FEP. The results show that the specific degassing rate (K) was 2.3 times faster at the higher temperature.

The degassing rate constant (K) also provides a means of estimating the contaminant concentration at any time if the area of the exposed elastomers is known. This can be done by multiplying (K) by the concentration at time (t) and this value is multiplied by the area of exposed elastomers. The concentration at time (t) is obtained from the figures. The value from the above calculations would be divided by the weight of the nitrogen in the system to estimate the concentration of contaminant in the entire system which could be stated in parts per million.

The degassing rate from the elastomers was described by numerical values of  $\underline{K}$ . It may also be described by giving the period of half life; that is, the time necessary for half of the contaminant to diffuse from the elastomer. This will give an indication of the time required for decontamination. The half-life equation is derived by substituting  $1/2$  into (2) as follows:

$$K = \frac{2.303}{t_{\frac{1}{2}}} \log \frac{1}{\frac{1}{2}} = \frac{0.693}{t_{\frac{1}{2}}}$$

Rearranging the above equation, the half life in a first-order equation is then:

$$t_{\frac{1}{2}} = \frac{0.693}{K} \quad (4)$$

The half-life determination provides a way to estimate the time required to reduce the concentration of the contaminants in the elastomers to an acceptable level. The half-life time values do not imply that all of the contaminants would be removed by doubling the time. The first-order equation shows that the amount of degassing is proportional to the amount present. To use an example, if the initial concentration was  $4.0 \text{ mg/cm}^2$  and the half life was 60 minutes, in an hour the concentration would be  $2.0 \text{ mg/cm}^2$ ; and, at the end of the second hour, the concentration would be reduced to  $1.0 \text{ mg/cm}^2$ .

#### 1. Environmental and Temperature Effect

The results show that the rate the contaminants degas from the elastomers is independent of its environment at the same conditions. The degassing rate constants (K), which are shown in Table 2-XV, show, for the initial degassing of  $\text{N}_2\text{O}_4$  from Teflon<sup>®</sup> FEP, values of  $1.4 \times 10^{-3}$ ,  $1.5 \times 10^{-3}$ , and  $1.8 \times 10^{-3}$  in environments of  $\text{GN}_2$ , Freon<sup>®</sup> TF, and carbon tetrachloride. There is no significant difference in the above values. The degassing of Aerozine-50 from Stillman rubber at ambient conditions in environments of  $\text{GN}_2$  and methanol shows the rates were approximately identical. The (K) value shown in Table 2-XVI is  $3.06 \times 10^{-4}$  for both the  $\text{GN}_2$  and methanol.

The rate at which the contaminants degas is temperature-dependent. An increase in temperature significantly increases the degassing rate. The degassing of  $\text{N}_2\text{O}_4$  from Teflon<sup>®</sup> FEP shows K values of  $1.4 \times 10^{-3}$ ,  $3.4 \times 10^{-3}$ , and  $1.1 \times 10^{-2}$  obtained from the tests using  $\text{GN}_2$  purge made at temperatures of  $25^\circ$ ,  $65^\circ$ , and  $100^\circ \text{ C}$  were plotted on a semi-log graph and gave a reasonable fit. This means that as the temperature is increased, the degassing rate is increased exponentially. This is illustrated in Figure 2-14.

Using Equation (4), the half life was determined for the degassing of  $\text{N}_2\text{O}_4$  from Teflon<sup>®</sup> FEP at temperatures of  $25^\circ \text{ C}$ ,  $65^\circ \text{ C}$ , and  $100^\circ \text{ C}$ . The above equation was also used for determining the half life for the degassing of Aerozine-50 from Stillman rubber. The results are shown below:

Temperature $^\circ\text{C}$	Half Life $\text{N}_2\text{O}_4$ From Teflon <sup>®</sup> FEP Minutes	Half Life A-50 From Stillman SR634-70, Minutes
25	490	2,260
65	240	295
90		70
100	63	
119		36

It is obvious from the above results that the degassing rate of the contaminant from the elastomers is temperature dependent.

E. Allowable Concentration of A-50 in Cleaning Solvent

Two tests were made to determine the concentration of A-50 that can be tolerated in the cleaning solvent and still effectively remove the contaminant from the elastomer. The first test was made using an A-50 concentration of approximately 9,000 ppm in methanol, and the concentration of the second test was 90 ppm. The procedure used was as follows: Three 500-ml round-bottomed flasks, equipped with a heating mantle and reflux condenser, were set up. Approximately 250 ml of the 9,000 ppm solution were placed in each flask. Four specimens of Stillman rubber which had been immersed in A-50 for several hours were placed in the first flask. Four specimens of rubber which had not been exposed to A-50 were placed in the second flask. The third flask was used as a control with uncontaminated solvent in it. After placing the specimens in the flasks, heat was applied, and the temperature of the solutions was raised to the boiling point. The solutions were boiled for 16 hours while maintaining total reflux. The specimens were removed from the solutions after this time and weighed. The A-50 content was determined for each flask. The rubber specimens were then placed in the metal test chamber, and steam was passed through the chamber for several hours. The exit steam from the test chamber was discharged into a condenser and the A-50 content of the condensate determined. The specimens previously exposed to the A-50 and the specimens which had not been exposed to the A-50 were steam-treated separately.

The three different solutions (that which contained specimens exposed to A-50, specimens not exposed to A-50, and the control) show practically no difference in the A-50 concentration. This indicates that the rubber is not selective for the fuel and further substantiates the hypothesis that the propellants are absorbed and not chemically adsorbed into the elastomers. Very little A-50 was extracted by the steam treatment--approximately two milligrams from the specimens preexposed to the A-50, and about one milligram from the specimens not exposed to the A-50.

The test using 90 ppm A-50 in the methanol was carried out as described above with the exception that the specimens were not subjected to the steam treatment after they were refluxed. The most significant results shown by this test were that most A-50 contained in the preexposed specimens was extracted during the 16 hours of boiling under reflux.

The major conclusion drawn from these tests is that the solvent can tolerate several hundred parts per million of the contaminant and still effectively extract the contaminant from the elastomer. More work should be done in this area.

## F. Tables

TABLE 2-I SOLVENTS USED IN THE SCREENING TESTS

Solvent	Service		Compatibility Test	
	Oxidant	Fuel	Propellant	Elastomer
Tribromofluoromethane	X		Compatible	Failed
Trichlorofluoromethane (Freon® MF)	X	X	Both Compatible	Compatible
Dibromodifluoromethane	X		Compatible	
Difluorotetrachloroethane (Freon® 112) Mixed Isomer	X		Compatible	
1,1-Dichloro-2,2,2-Trifluoroethane (Freon® 123)	X		Compatible	Failed
1,1-Dibromo-2,2,2-Trifluoroethane	X		Compatible	
1,2-Dibromo-1,2,2-Tetrafluoroethane	X	X	Both Compatible	Compatible
1,1,2-Trichloro-1,2,2-Trifluoroethane (Freon® TF)	X		Compatible	
Perfluorocyclobutane (Freon® C-318)	X		Compatible	
Perfluorodimethylcyclobutane	X	X	Compatible	Compatible
Freon® E-2	X		Failed	
Dibromochloromethane	X	X	Compatible	
Methylene Chloride	X	X	Both Compatible	
Chloroform	X	X	Failed (ox)	Compatible
Bromochloromethane	X	X	Compatible (fuel)	
Carbon Tetrachloride	X		Compatible	Compatible
Bromodichloromethane	X		Compatible	Failed
1,1,1-Trichloroethane	X		Failed	
Trichloroethylene	X		Failed	
Tetrachloroethylene	X		Failed	
Methylene Bromide	X		Failed	
Formamide		X		Compatible
Methanol		X	Compatible	Compatible
Ethanol		X	Compatible	Failed
Acetone		X	Failed	Failed
2,2-Dichloro-1,1-Difluoromethyl ethyl ether	X		Failed	Compatible
n-Propanol		X		Compatible
Isopropanol		X		Compatible
Isobutanol		X		Compatible
Secondary Butanol		X		Compatible
1,2-Butylene Oxide		X		Compatible
1,4-Dioxane		X		Compatible
Pentane				Failed
Benzene				Failed
Cyclohexane				Failed
Hexane				Failed
Iso-octane				Failed
Nitrogen				Compatible
Steam				Compatible

TABLE 2-II THERMODYNAMIC CALCULATION RESULTS

Reaction	$\Delta H$ Kcal	$\Delta H$ Kcal Per g N <sub>2</sub> O <sub>4</sub>	$\Delta H$ Kcal Per Mol Solvent	$\Delta F$ Kcal	$\Delta F$ Kcal Per g N <sub>2</sub> O <sub>4</sub>	$\Delta F$ Kcal Per Mol Solvent
N <sub>2</sub> O <sub>4</sub> + 8HCl → 4H <sub>2</sub> O + N <sub>2</sub> + 4Cl <sub>2</sub>	- 50.6	-0.55	- 6.3	- 61.1	-0.657	- 7.64
N <sub>2</sub> O <sub>4</sub> + 2 CCl <sub>3</sub> F → 2CO <sub>2</sub> + F <sub>2</sub> + Cl <sub>2</sub> + N <sub>2</sub>	- 41.4	-0.45	- 20.7	- 88.9	-0.967	- 44.45
5/4N <sub>2</sub> O <sub>4</sub> + 2CHCl <sub>2</sub> F → 2CO <sub>2</sub> + H <sub>2</sub> O + Cl <sub>2</sub> + F <sub>2</sub> 5/4N <sub>2</sub>	-102.1	-1.01	- 51.0	-149.0	-1.62	- 74.6
N <sub>2</sub> O <sub>4</sub> + 2CCl <sub>4</sub> → 2CO <sub>2</sub> + 4Cl <sub>2</sub> + N <sub>2</sub>	-136.0	-1.5	- 63.0	-184.0	-2.0	- 92.0
5/4N <sub>2</sub> O <sub>4</sub> + 2CHCl <sub>3</sub> → 2CO <sub>2</sub> + H <sub>2</sub> O + 3O <sub>2</sub> + 5/4N <sub>2</sub>	-191.0	-1.7	- 95.0	-238.0	-2.1	-119.0
3/4N <sub>2</sub> O <sub>4</sub> + CH <sub>2</sub> Cl <sub>2</sub> → CO <sub>2</sub> + H <sub>2</sub> O + Cl <sub>2</sub> + 3/4N <sub>2</sub>	-126.0	-1.8	-126.0	-150.0	-2.3	-151.0
N <sub>2</sub> O <sub>4</sub> + 2N <sub>2</sub> H <sub>2</sub> → 4H <sub>2</sub> O + 3 N <sub>2</sub>	-272.0	-3.0	-136.0	-308.0	-3.3	-154.0
5/4N <sub>2</sub> O <sub>4</sub> + 2HCN → 2CO <sub>2</sub> + H <sub>2</sub> O + 5/4N <sub>2</sub>	-303.0	-2.6	-152.0	-324.0	-2.8	-162.0
N <sub>2</sub> O <sub>4</sub> + C <sub>2</sub> Cl <sub>4</sub> → 2CO <sub>2</sub> + 2Cl <sub>2</sub> + N <sub>2</sub>	-181.0	-2.0	-181.0	-208.0	-2.3	-208.0
9/4N <sub>2</sub> O <sub>4</sub> + 2C <sub>2</sub> HCl <sub>3</sub> → 4CO <sub>2</sub> + H <sub>2</sub> O + 3Cl <sub>2</sub> + 9/4N <sub>2</sub>	-422.0	-2.0	-211.0	-494.0	-2.4	-247.0
5/4N <sub>2</sub> O <sub>4</sub> + C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> → 2CO <sub>2</sub> + H <sub>2</sub> O + Cl <sub>2</sub> + 5/4N <sub>2</sub>	-240.0	-2.1	-240.0	-271.0	-2.4	-271.0

TABLE 2-III

## RESULTS OF SOLVENT-ELASTOMER COMPATIBILITY STUDY

<u>Solvents</u>	<u>Elastomers</u>					
	<u>Teflon<sup>®</sup> TFE</u>	<u>Teflon<sup>®</sup> FEP</u>	<u>Kel-F No. 300</u>	<u>Kynar</u>	<u>Rulon</u>	<u>Stillman SR634-70 Rubber</u>
Ethanol	10 Wks Compat	8 Wks Compat	10 Wks Compat	No Test	5 Wks Compat	5 Wks Compat
Methanol	10 Wks Compat	8 Wks Compat	10 Wks Compat	5 Wks Compat	5 Wks Compat	5 Wks Compat
Acetone	10 Wks Compat	8 Wks Compat	10 Wks Compat	No Test	No Test	1 Wk Failed
90% Hexane 10% Aerozine-50	9 Wks Compat	No Test	9 Wks Compat	No Test	No Test	No Test
Aerozine-50	9 Wks Compat	8 Wks Compat	3 Wks Failed	5 Wks Compat	5 Wks Compat	5 Wks Failed
Freon <sup>®</sup> 11	8 Wks Compat	8 Wks Compat	4 Wks Compat	5 Wks Compat	5 Wks Compat	No Test
90% Freon <sup>®</sup> 11 10% N <sub>2</sub> O <sub>4</sub>	8 Wks Compat	8 Wks Compat	1 Wk Failed	No Test	No Test	No Test
Freon <sup>®</sup> 113	8 Wks Compat	8 Wks Compat	8 Wks Failed	No Test	No Test	No Test
90% Freon <sup>®</sup> 113 10% N <sub>2</sub> O <sub>4</sub>	8 Wks Compat	8 Wks Compat	1 Wk Failed	No Test	No Test	No Test
Bromo-chloro Methane	8 Wks Compat	8 Wks Compat	8 Wks Compat	No Test	No Test	No Test
90% Bromo-chloro Methane 10% N <sub>2</sub> O <sub>4</sub>	No Test	8 Wks Compat	No Test	No Test	No Test	No Test
N <sub>2</sub> O <sub>4</sub>	8 Wks Compat	8 Wks Compat	1 Wk Failed	5 Wks Compat	5 Wks Compat	No Test
Bromo-dichloro Methane	4 Wks Compat	4 Wks Compat	No Test	4 Wks Compat	4 Wks Compat	1 Wk Failed
Tribromo-fluoro Methane	4 Wks Compat	4 Wks Compat	No Test	4 Wks Compat	4 Wks Compat	1 Wk Failed



TABLE 2-III  
(CONTINUED)

RESULTS OF SOLVENT-ELASTOMER COMPATIBILITY STUDY

<u>Solvents</u>	<u>Elastomers</u>					<u>Stillman SR634-70 Rubber</u>
	<u>Teflon<sup>®</sup> TFE</u>	<u>Teflon<sup>®</sup> FEP</u>	<u>Kel-F No. 300</u>	<u>Kynar</u>	<u>Rulon</u>	
1,1 Dibromo-2,2,2 trifluoro Ethane	4 Wks Compat	4 Wks Compat	No Test	4 Wks Compat	4 Wks Compat	1 Wk Failed
2,2-Dichloro-1,1-difluoro Ethyl Methyl Ether	No Test	No Test	No Test	1 Wk Compat	No Test	1 Wk Failed
Carbon Tetrachloride	No Test	No Test	No Test	No Test	1 Wk Compat	No Test
Isopropyl Alcohol	No Test	No Test	No Test	No Test	No Test	1 Wk Compat
Cyclohexane	No Test	No Test	No Test	No Test	No Test	1 Wk Failed
Iso-Octane	No Test	No Test	No Test	No Test	No Test	1 Wk Failed
Benzene	No Test	No Test	No Test	No Test	No Test	1 Wk Failed

TABLE 2-IV

REMOVAL OF  $N_2O_4$  FROM TEFLON<sup>®</sup> FEP IN VARIOUS SOLVENTS

Time	Freon <sup>®</sup> MF		Freon <sup>®</sup> TF		Carbon Tetrachloride	
	$N_2O_4$ mg/cm <sup>2</sup>	% $N_2O_4$ Retained	$N_2O_4$ mg/cm <sup>2</sup>	% $N_2O_4$ Retained	$N_2O_4$ mg/cm <sup>2</sup>	% $N_2O_4$ Retained
0	0.89	-	2.11	-	2.57	-
15 min.	0.829	93.2	1.967	93.1	2.35	91.4
30 min.	0.828	93.1	1.925	91.2	2.28	88.7
60 min.	0.801	90.0	1.832	86.8	2.145	83.3
120 min.	0.78	87.6	1.74	82.4	2.08	80.5
240 min.	0.721	80.9	1.64	75.7	1.97	76.6
24 hrs.	-	-	1.267	60.0	1.31	51.0

TABLE 2-V

REMOVAL OF  $N_2O_4$  FROM TEFLON<sup>®</sup> TFE IN VARIOUS SOLVENTS

Time	Freon <sup>®</sup> MF		Freon <sup>®</sup> TF		Carbon Tetrachloride	
	$N_2O_4$ mg/cm <sup>2</sup>	% $N_2O_4$ Retained	$N_2O_4$ mg/cm <sup>2</sup>	% $N_2O_4$ Retained	$N_2O_4$ mg/cm <sup>2</sup>	% $N_2O_4$ Retained
0	2.44	-	1.65	-	2.6	-
15 min.	2.23	91.3	1.34	81.0	2.18	83.9
30 min.	2.18	89.2	1.45	88.0	2.15	83.7
60 min.	2.12	87.0	1.315	79.8	2.01	77.4
120 min.	1.97	80.6	1.26	76.3	1.82	70.0
240 min.	1.81	74.2	1.144	69.3	1.49	57.4
24 hrs.	1.67	68.4	0.895	54.3	1.195	45.8

TABLE 2-VI

REMOVAL OF  $N_2O_4$  FROM RULON USING VARIOUS SOLVENTS

Time Min.	Carbon Tetrachloride		Freon <sup>®</sup> MF		Nitrogen Purge	
	$N_2O_4$ mg/cm <sup>2</sup>	% $N_2O_4$ Retained	$N_2O_4$ mg/cm <sup>2</sup>	% $N_2O_4$ Retained	Time	$N_2O_4$ mg/cm <sup>2</sup> % $N_2O_4$ Retained
0	6.93	-	4.5	-	0	5.07      -
15	5.68	82.8	3.89	86.3	15 min.	4.54      89.7
30	5.48	79.0	3.72	82.6	45 min.	4.22      83.2
60	5.39	77.7	3.39	75.2	75 min.	4.01      79.1
120	5.08	73.2	3.15	70.0	135 min.	3.77      74.4
240	4.48	64.7	2.45	54.4	165 min.	3.59      70.8
					195 min.	3.41      67.2
					28 hrs.	2.05      40.5

TABLE 2-VII

REMOVAL OF N<sub>2</sub>O<sub>4</sub> FROM KYNAR USING VARIOUS SOLVENTS

Ambient Temperature

Time	Freon <sup>®</sup> MF		Carbon Tetrachloride		Nitrogen Purge		
	N <sub>2</sub> O <sub>4</sub> mg/cm <sup>2</sup>	% N <sub>2</sub> O <sub>4</sub> Retained	N <sub>2</sub> O <sub>4</sub> mg/cm <sup>2</sup>	% N <sub>2</sub> O <sub>4</sub> Retained	Time	N <sub>2</sub> O <sub>4</sub> mg/cm <sup>2</sup>	% N <sub>2</sub> O <sub>4</sub> Retained
0	11.2	-	11.06	-	0	5.62	-
15 min.	10.62	94.8	9.41	85.0	30 min.	4.65	82.2
30 min.	10.58	94.5	9.48	85.6	75 min.	4.39	77.1
60 min.	10.18	91.0	8.9	80.4	165 min.	4.07	72.3
120 min.	9.89	88.1	8.5	83.8	380 min.	3.79	67.4
240 min.	9.46	84.4	8.37	75.6			
24 hrs.	8.69	68.7	6.97	63.0	24 hrs.	2.9	51.6

TABLE 2-VIII

REMOVAL OF N<sub>2</sub>O<sub>4</sub> FROM ELASTOMERS, PURGING WITH GN<sub>2</sub>

<u>Time</u>	<u>Teflon<sup>®</sup> FEP Ambient</u>		<u>Teflon<sup>®</sup> FEP 65° C</u>		<u>Teflon<sup>®</sup> TFE 65° C</u>	
	<u>mg/cm<sup>2</sup></u>	<u>% N<sub>2</sub>O<sub>4</sub> Retained</u>	<u>mg/cm<sup>2</sup></u>	<u>% N<sub>2</sub>O<sub>4</sub> Retained</u>	<u>mg/cm<sup>2</sup></u>	<u>% N<sub>2</sub>O<sub>4</sub> Retained</u>
0	2.060		5.345		2.44	
20 min.			4.19	78.4		
30 min.	1.481	70.1			1.467	59.8
40 min.			3.94	73.6		
1.0 hr.			3.61	67.5		
1.33 hrs.	1.385	67.2			1.3	53.2
2.0 hrs.			2.94	55.0		
2.75 hrs.	1.230	59.7			1.04	42.6
6.33 hrs.	1.055	51.2			.743	30.2
19.0 hrs.			.785	14.6		
24.0 hrs.	.710	34.4	.524	9.8	.275	11.3

TABLE 2-IX

REMOVAL OF N<sub>2</sub>O<sub>4</sub> FROM TEFLON<sup>®</sup> TFE AND FEP  
AT A TEMPERATURE OF 100° C USING GN<sub>2</sub>

<u>Time Min.</u>	<u>TFE</u>		<u>FEP</u>	
	<u>N<sub>2</sub>O<sub>4</sub> mg/cm<sup>2</sup></u>	<u>% N<sub>2</sub>O<sub>4</sub> Retained</u>	<u>N<sub>2</sub>O<sub>4</sub> mg/cm<sup>2</sup></u>	<u>% N<sub>2</sub>O<sub>4</sub> Retained</u>
0	1.77	-	5.39	-
30	0.44	24.8	2.62	48.6
60	0.34	19.2	1.85	34.3
90	0.27	15.2	1.28	23.7

TABLE 2-X

REMOVAL OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER  
USING VARIOUS SOLVENTS

Time Min.	Iso-Octane		Benzene		Formamide	
	A-50 mg/cm <sup>2</sup>	% A-50 Retained	A-50 mg/cm <sup>2</sup>	% A-50 Retained	A-50 mg/cm <sup>2</sup>	% A-50 Retained
0	4.14	-	3.98	-	5.11	-
30	3.98	96.0	2.45	61.4	5.10	99.7
60	3.89	94.0	2.16	54.2	5.09	99.6
120	3.68	88.9	2.1	52.7	5.07	99.3
180	3.35	80.9	2.7	67.8	5.05	98.9

TABLE 2-XI

REMOVAL OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER  
USING METHANOL AND WATER .

Time Min.	Methanol		Water	
	A-50 mg/cm <sup>2</sup>	% A-50 Retained	A-50 mg/cm <sup>2</sup>	% A-50 Retained
0	7.42	-	7.55	-
30	7.3	98.3	7.35	97.4
60	7.23	97.4	7.30	96.7
90	7.16	96.4	7.29	96.5
120	7.10	95.7	7.24	95.9
180	7.01	94.4	7.17	95.0
210	6.95	93.7	7.17	95.0
240			7.17	95.0

TABLE 2-XII

REMOVAL OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER  
USING GN<sub>2</sub> PURGE AT 25° AND 90° C

25° C			90° C		
<u>Time</u> <u>Min.</u>	<u>A-50</u> <u>mg/cm<sup>2</sup></u>	<u>% A-50</u> <u>Retained</u>	<u>Time</u> <u>Min.</u>	<u>A-50</u> <u>mg/cm<sup>2</sup></u>	<u>% A-50</u> <u>Retained</u>
0	7.21	-	0	6.34	-
30	7.13	98.8	10	3.61	56.9
60	7.04	97.5	20	2.31	36.6
90	6.98	96.8	40	1.28	20.2
120	6.92	95.9	60	1.07	16.9
180	6.82	94.6	80	0.861	13.6
210	6.77	93.9	24 hrs.	0.0	0
240	6.71	93.1			

TABLE 2-XIII

REMOVAL OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER  
USING METHANOL AND ISOBUTANOL VAPORS AT 65° AND 100° C

<u>Time</u> <u>Min.</u>	<u>Methanol Vapors</u>		<u>Isobutanol Vapors</u>	
	<u>A-50</u> <u>mg/cm<sup>2</sup></u>	<u>% A-50</u> <u>Retained</u>	<u>A-50</u> <u>mg/cm<sup>2</sup></u>	<u>% A-50</u> <u>Retained</u>
0	7.38	-	7.89	-
30	6.68	90.4	7.24	86.3
60	6.08	82.3	6.17	73.5
90	5.66	76.7	5.34	63.7
120	5.28	72.5	5.14	61.2
150	4.96	67.1	4.52	53.9
180	4.69	63.5	3.84	45.7
210	4.5	60.9	3.58	42.6
240	2.44	60.2	3.48	41.5

TABLE 2-XIV

REMOVAL OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER  
USING 13 PSIG STEAM AT 119° C

<u>Time</u> <u>Min.</u>	<u>A-50</u> <u>mg/cm<sup>2</sup></u>	<u>% A-50</u> <u>Retained</u>
0	5.97	-
5.3	5.26	88.0
12.2	4.24	71.3
20.0	3.48	68.2
27.8	2.9	48.5
35.6	2.46	41.1
43.4	2.1	35.1
51.2	1.81	30.3
59.0	1.58	26.4
66.8	1.37	22.9
74.6	1.2	20.1
82.4	1.06	17.7
90.2	0.94	15.7
98.0	0.82	13.7
105.8	0.72	12.1
113.6	0.61	10.3
121.4	0.53	8.9
128.4	0.45	7.5
136.2	0.39	6.5
145.0	0.33	5.5
152.8	0.28	4.7
160.6	0.23	3.8
168.4	0.19	3.2
H <sub>2</sub> O Trap		2.5



TABLE 2-XV

DEGASSING RATE CONSTANTS FOR FREON <sup>(B)</sup>11 AND 113  
AND N<sub>2</sub>O<sub>4</sub> FROM ELASTOMERS

Elastomer	Condition	Degassing Rate K = mg/cm <sup>2</sup> /min.						
		Freon 11 GN <sub>2</sub> Purge Ambient	Freon 113 GN <sub>2</sub> Purge Ambient	N <sub>2</sub> O <sub>4</sub> GN <sub>2</sub> Purge Ambient	N <sub>2</sub> O <sub>4</sub> GN <sub>2</sub> Purge 65° C	N <sub>2</sub> O <sub>4</sub> in CCl <sub>3</sub> F	N <sub>2</sub> O <sub>4</sub> in CCl <sub>2</sub> F-CCl <sub>3</sub> F <sub>2</sub>	N <sub>2</sub> O <sub>4</sub> in CCl <sub>4</sub>
Teflon <sup>(B)</sup> FEP	K <sub>1</sub>	8.47 x 10 <sup>-4</sup>	1.1 x 10 <sup>-3</sup>	1.44 x 10 <sup>-3</sup>	3.4 x 10 <sup>-3</sup>	7.32 x 10 <sup>-4</sup>	1.56 x 10 <sup>-3</sup>	1.83 x 10 <sup>-3</sup>
	K <sub>2</sub>	5.2 x 10 <sup>-4</sup>	4.6 x 10 <sup>-4</sup>	3.7 x 10 <sup>-4</sup>	1.21 x 10 <sup>-3</sup>		7.1 x 10 <sup>-4</sup>	8.1 x 10 <sup>-4</sup>
Teflon <sup>(B)</sup> TFE	K <sub>1</sub>	9.08 x 10 <sup>-4</sup>	9.08 x 10 <sup>-4</sup>	2.7 x 10 <sup>-3</sup>		9.8 x 10 <sup>-4</sup>	3.24 x 10 <sup>-4</sup>	2.65 x 10 <sup>-3</sup>
	K <sub>2</sub>	1.0 x 10 <sup>-4</sup>	1.0 x 10 <sup>-4</sup>	5.9 x 10 <sup>-4</sup>				
Rulon	K <sub>1</sub>			2.2 x 10 <sup>-3</sup>		2.8 x 10 <sup>-3</sup>		1.08 x 10 <sup>-3</sup>
	K <sub>2</sub>			9.5 x 10 <sup>-4</sup>				3.9 x 10 <sup>-4</sup>
Kynar	K <sub>1</sub>					1.1 x 10 <sup>-3</sup>	1.4 x 10 <sup>-3</sup>	1.5 x 10 <sup>-3</sup>
	K <sub>2</sub>					3.2 x 10 <sup>-4</sup>	2.75 x 10 <sup>-4</sup>	8.8 x 10 <sup>-4</sup>

TABLE 2-XVI

DEGASSING RATE CONSTANTS K FOR AEROZINE-50  
 FROM STILLMAN SR634-70 RUBBER  
 AND FOR N<sub>2</sub>O<sub>4</sub> FROM TEFLONS<sup>®</sup> FEP AND TFE

	Stillman SR634-70 <u>Rubber</u>	Teflon <sup>®</sup> <u>FEP</u>	Teflon <sup>®</sup> <u>TFE</u>
GN <sub>2</sub> Ambient	3.06 x 10 <sup>-4</sup>		
Methanol Ambient	3.06 x 10 <sup>-4</sup>		
Methanol KSI	3.07 x 10 <sup>-3</sup>		
65° C (Vapor) KSII	2.34 x 10 <sup>-3</sup>		
Steam KSI	2.7 x 10 <sup>-2</sup>		
13 psig KSII	1.91 x 10 <sup>-2</sup>		
GN <sub>2</sub> KSI	3.51 x 10 <sup>-2</sup>		
90° C KSII	9.84 x 10 <sup>-3</sup>		
Isobutanol 100° C (Vapor)	3.78 x 10 <sup>-3</sup>		
Iso-octane Ambient	9.26 x 10 <sup>-4</sup>		
GN <sub>2</sub> K 100° C		1.1 x 10 <sup>-2</sup>	9.2 x 10 <sup>-3</sup>

G. Figures

Figure 2-1

DEGASSING OF FREON<sup>®</sup> 11 AND 113 FROM TEFLON<sup>®</sup> FEP  
USING NITROGEN PURGE

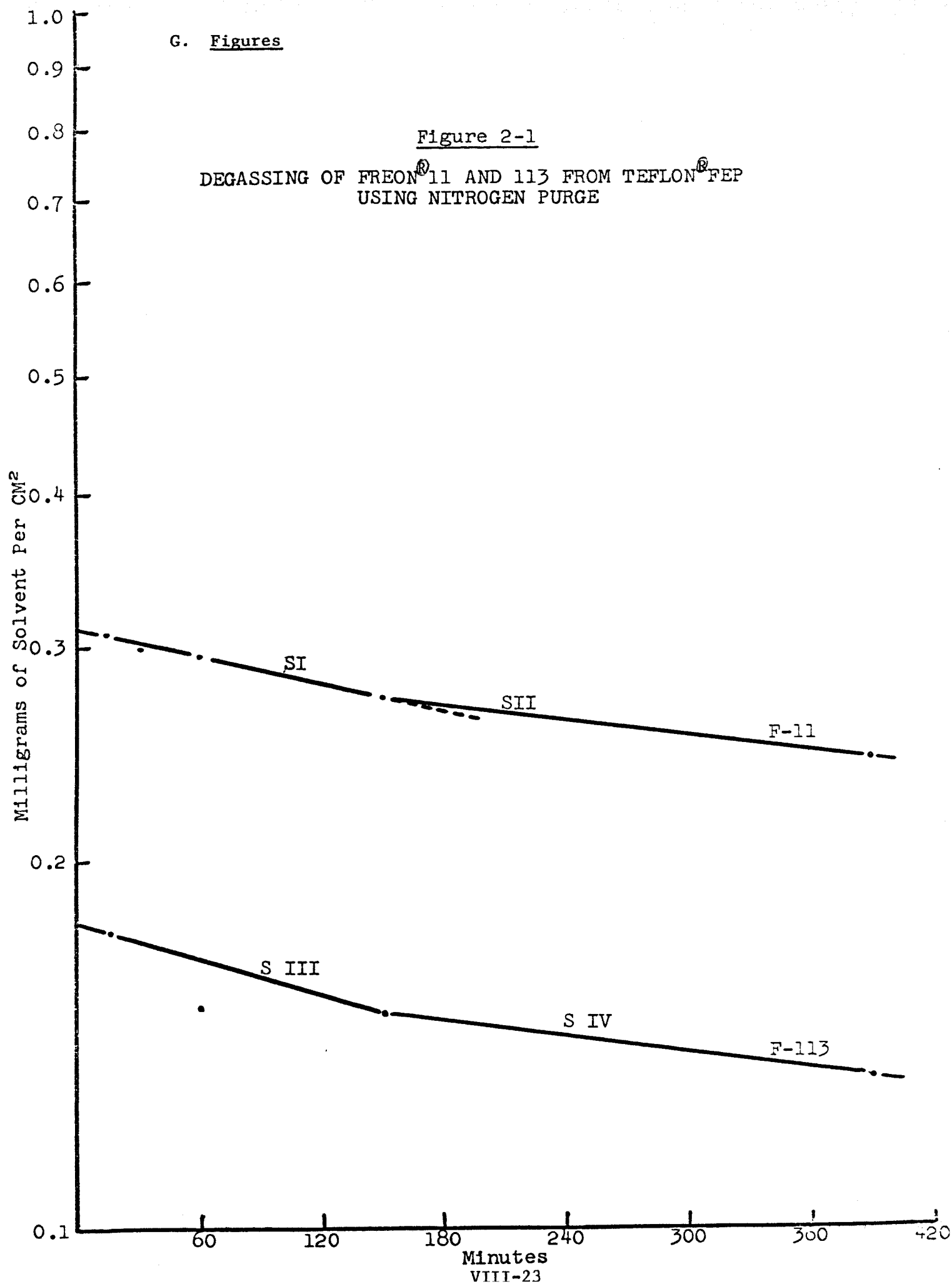
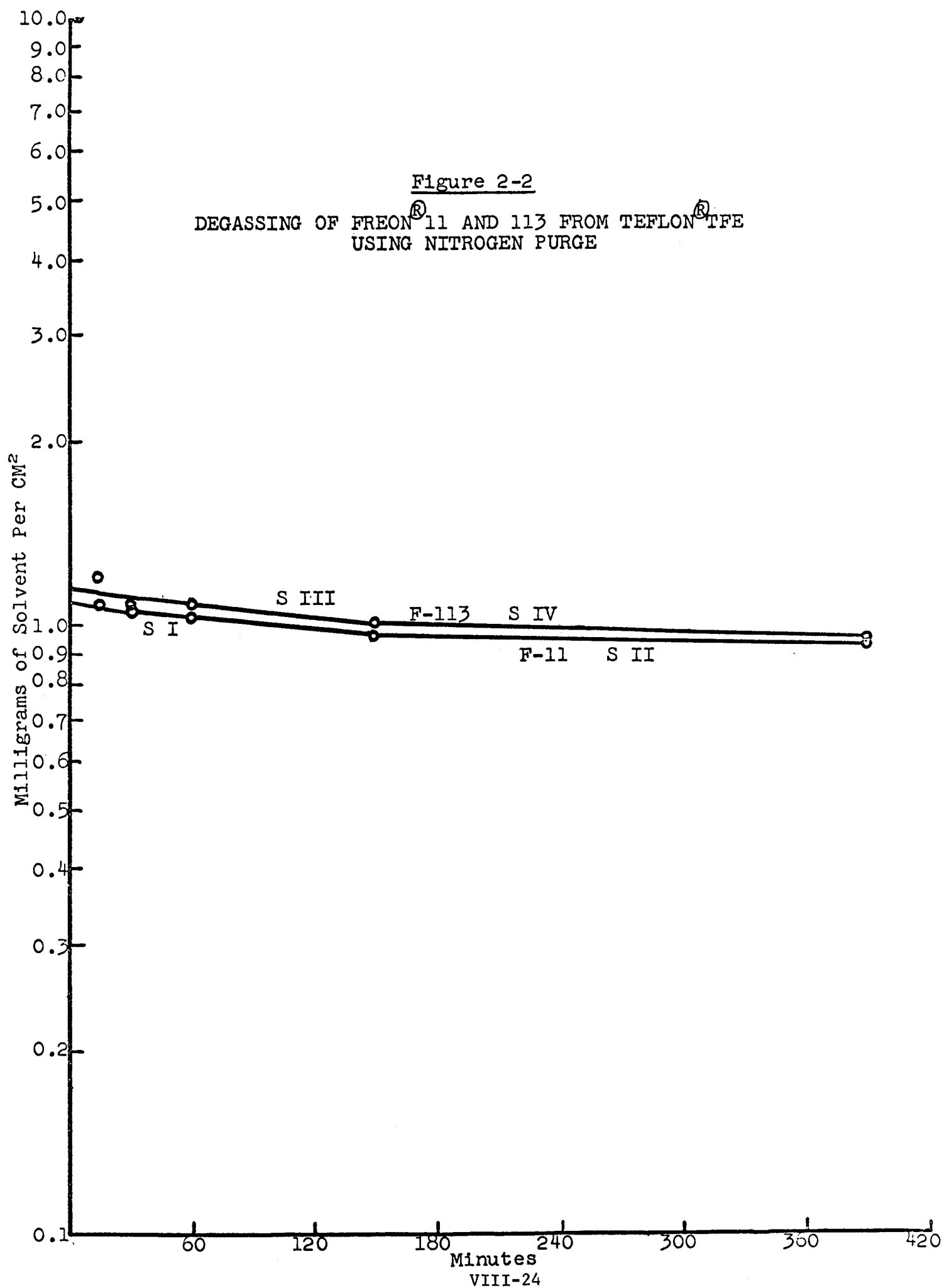
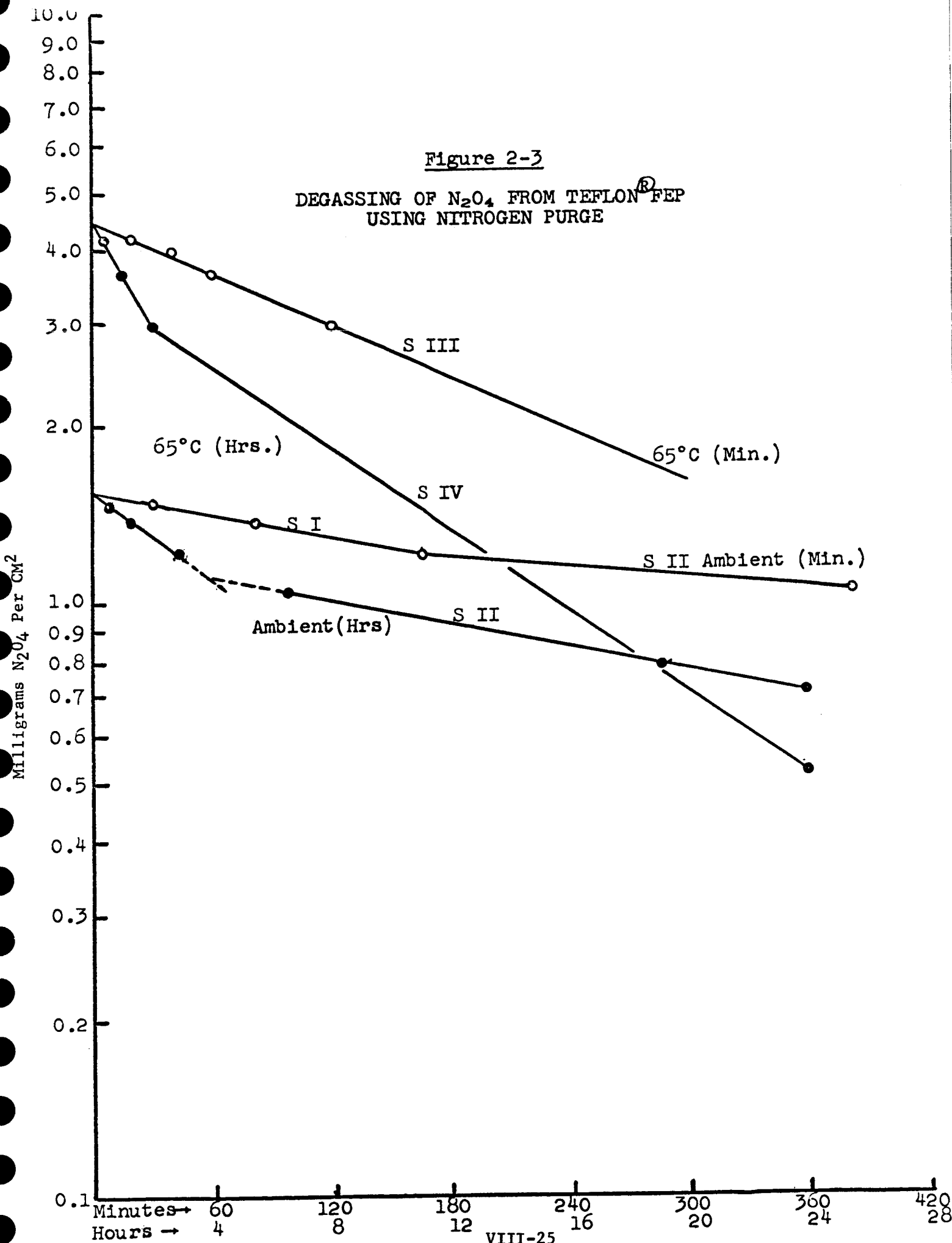


Figure 2-2

DEGASSING OF FREON<sup>®</sup> 11 AND 113 FROM TEFLON<sup>®</sup> TFE  
USING NITROGEN PURGE





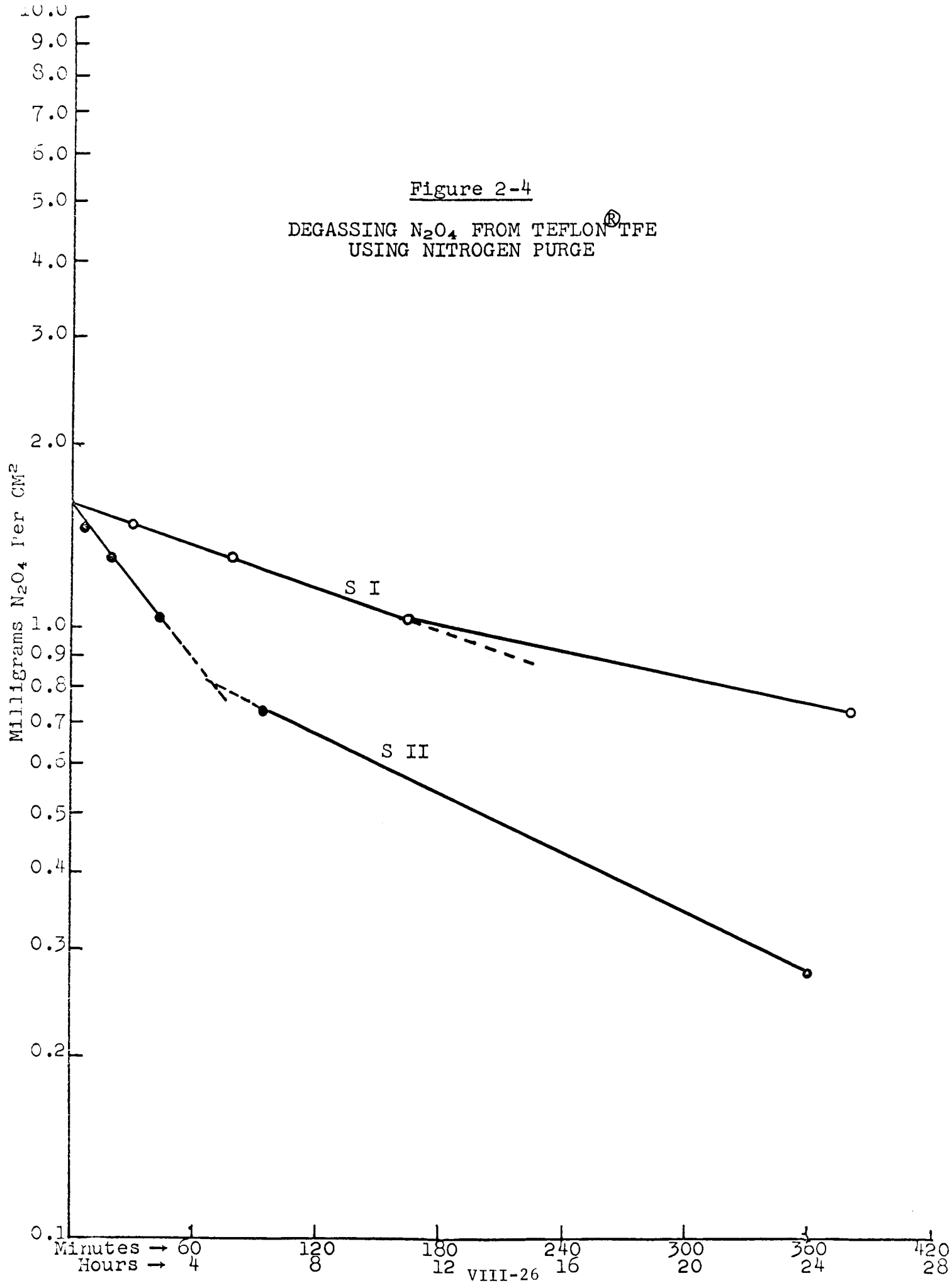
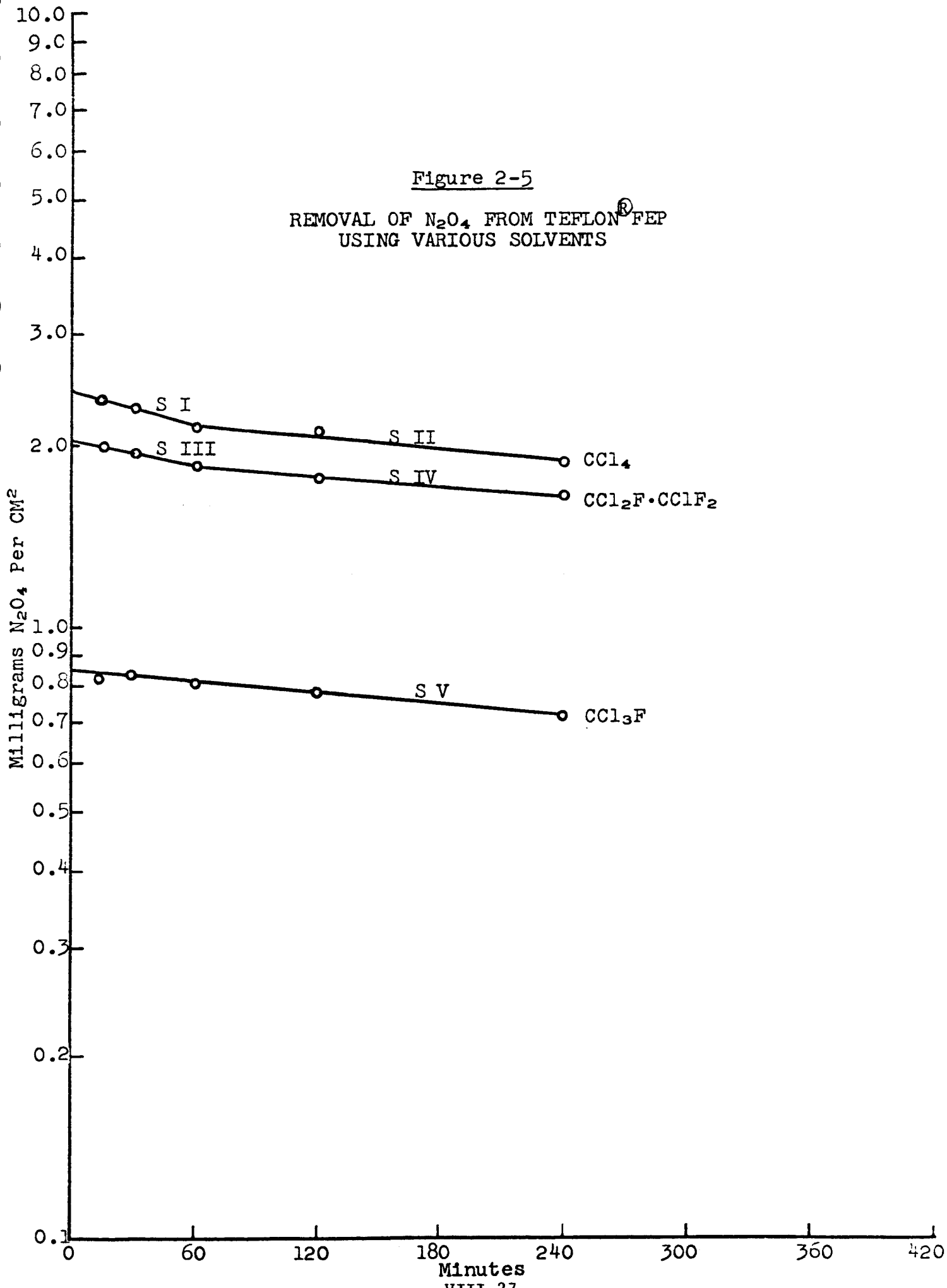


Figure 2-5

REMOVAL OF  $\text{N}_2\text{O}_4$  FROM TEFLON<sup>®</sup> FEP  
USING VARIOUS SOLVENTS



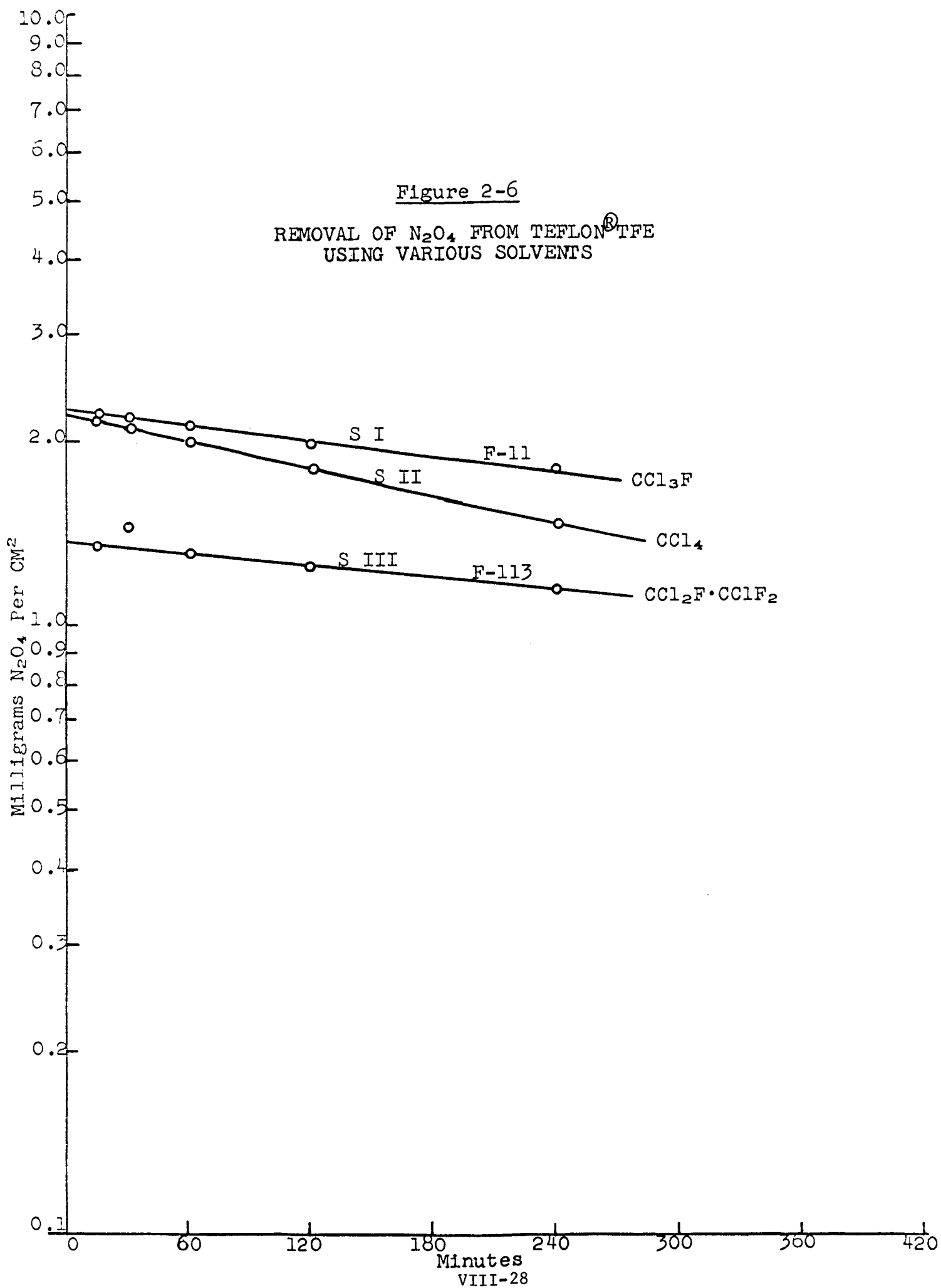
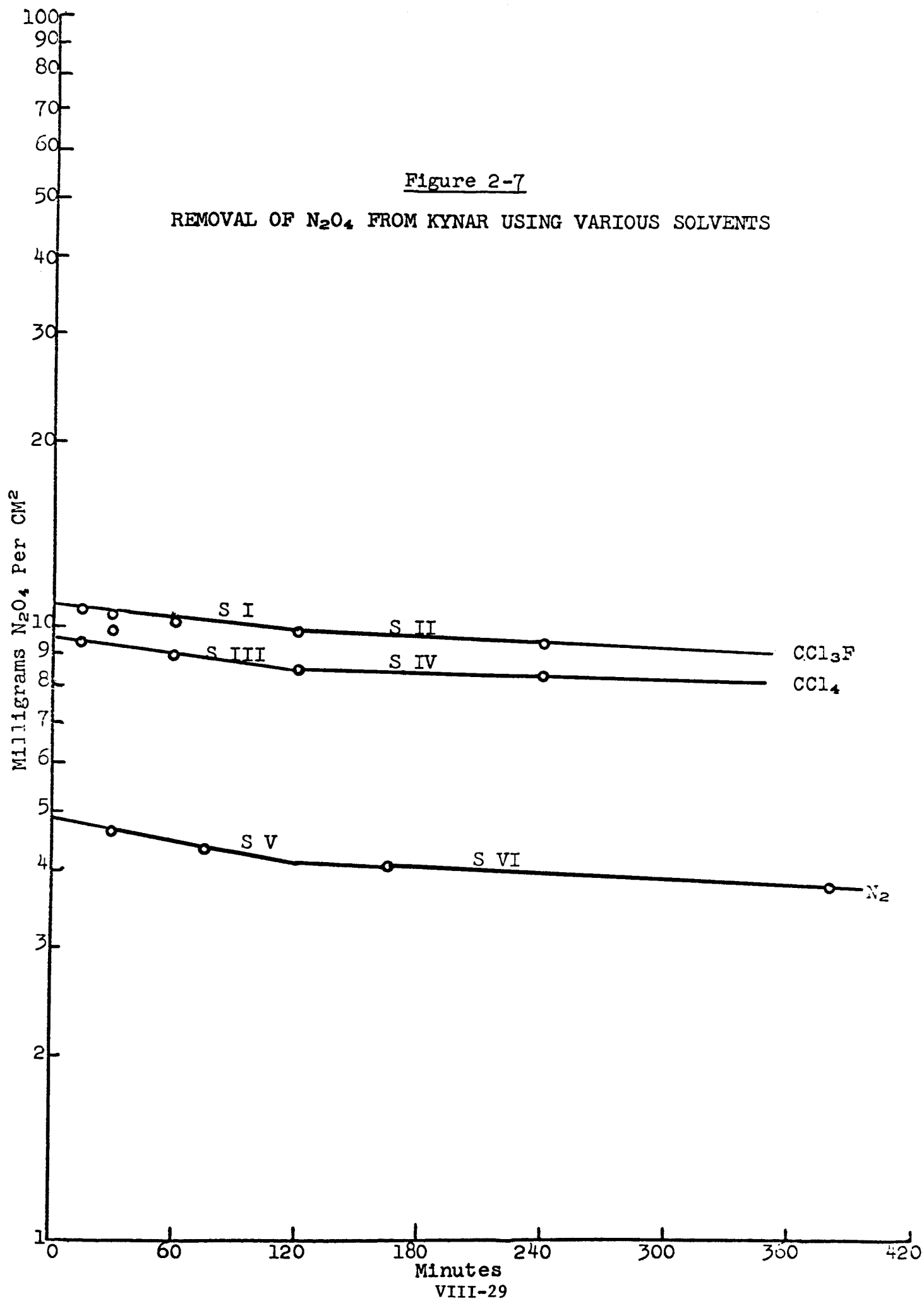




Figure 2-7

REMOVAL OF  $N_2O_4$  FROM KYNAR USING VARIOUS SOLVENTS



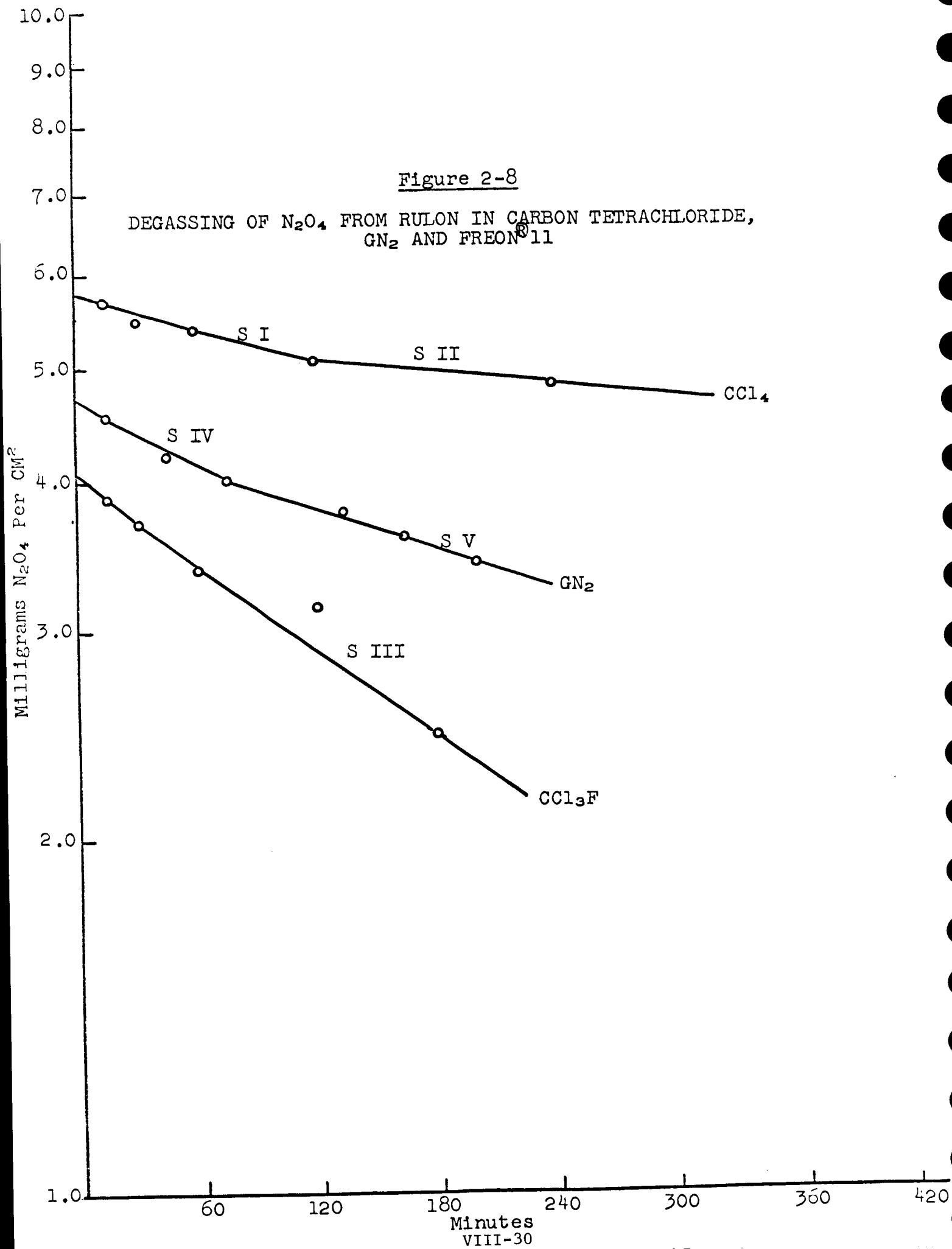


Figure 2-9

DEGASSING OF  $\text{N}_2\text{O}_4$  FROM TEFLON<sup>®</sup> TFE AT  $100^\circ\text{C}$ .  
IN GASEOUS NITROGEN STREAM

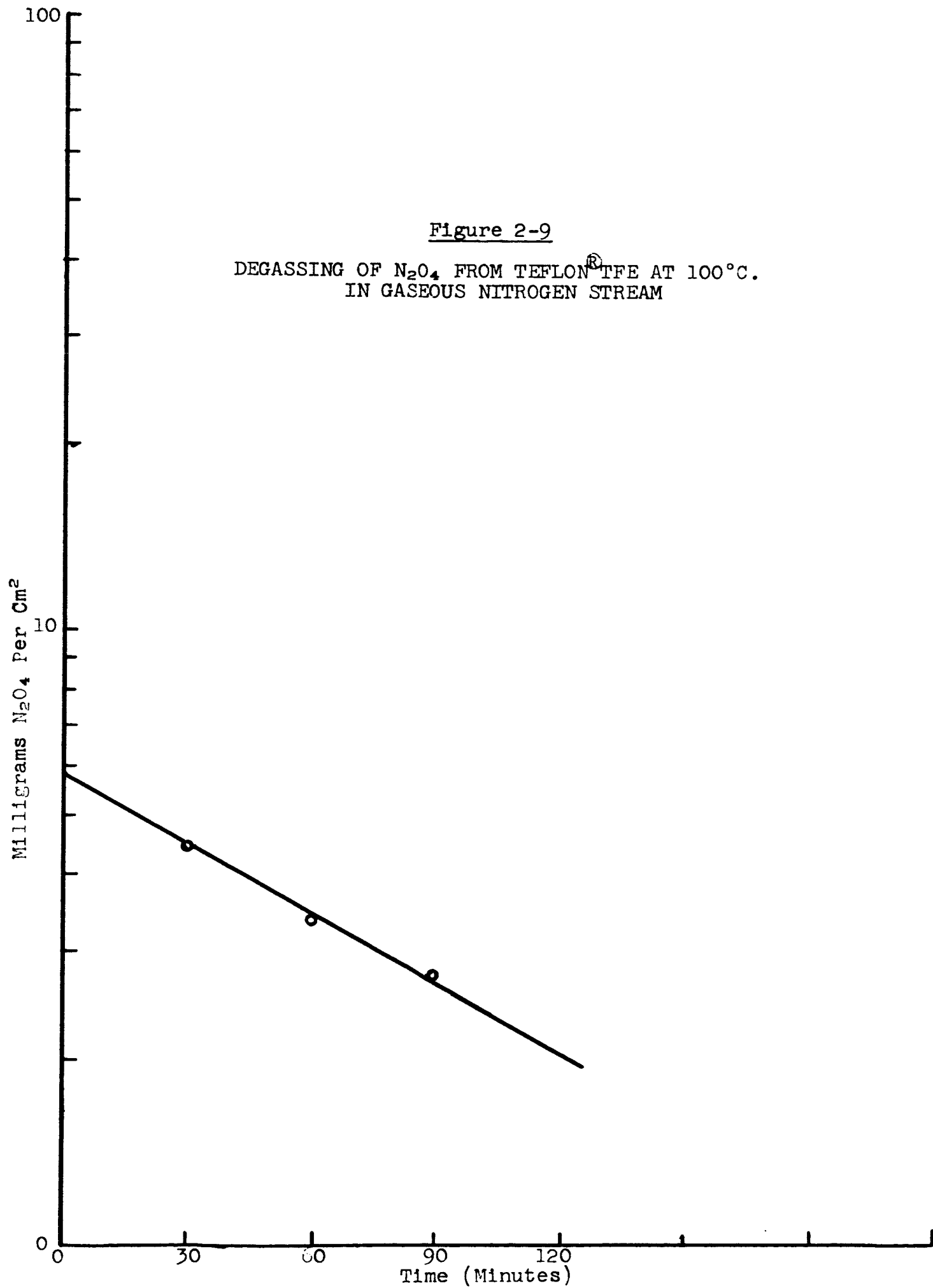


Figure 2-10

DEGASSING OF  $\text{N}_2\text{O}_4$  FROM TEFLON<sup>®</sup> FEP AT  $100^\circ\text{C}$ .  
IN GASEOUS NITROGEN STREAM

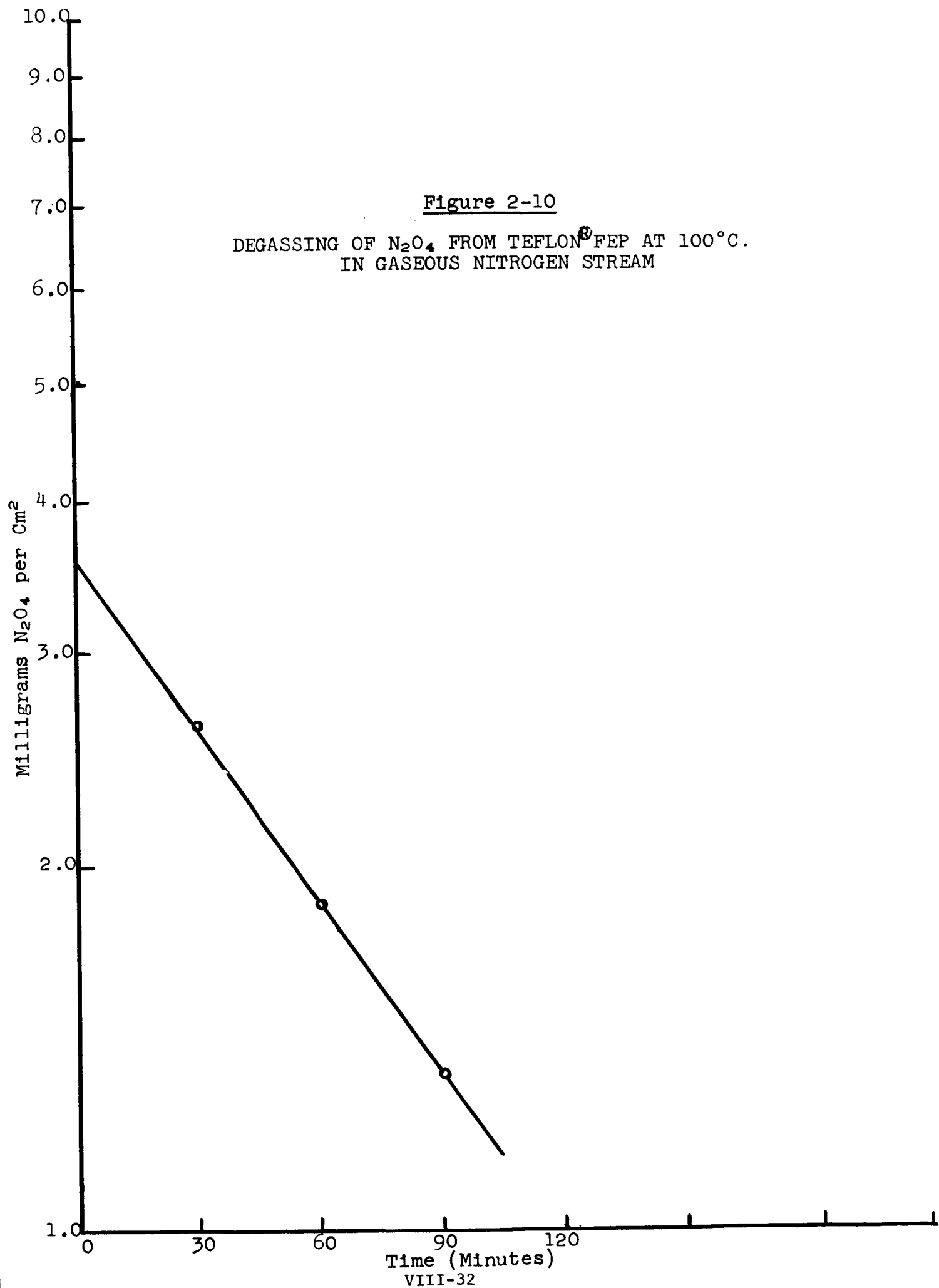


Figure 2-11

REMOVAL OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER

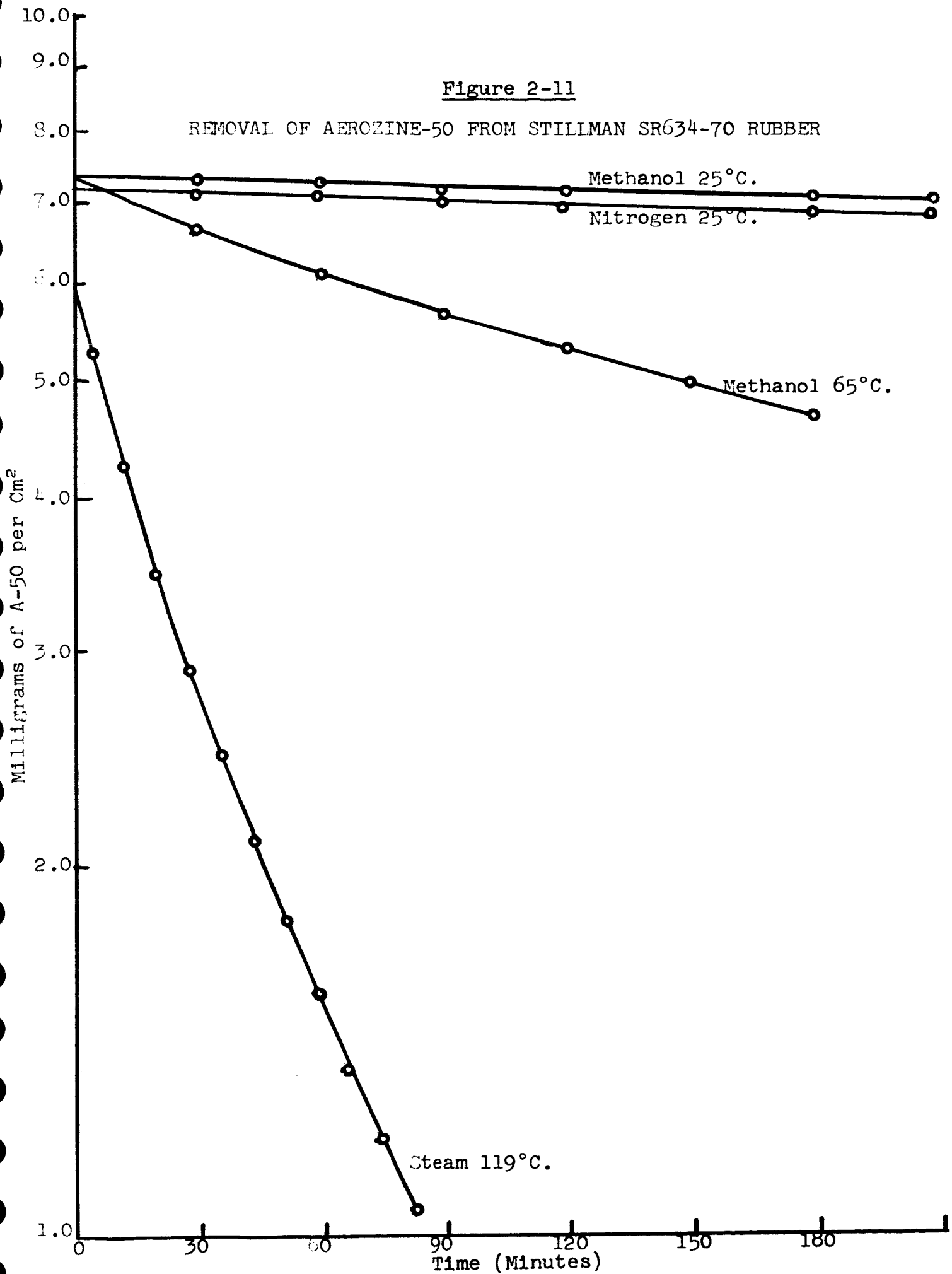
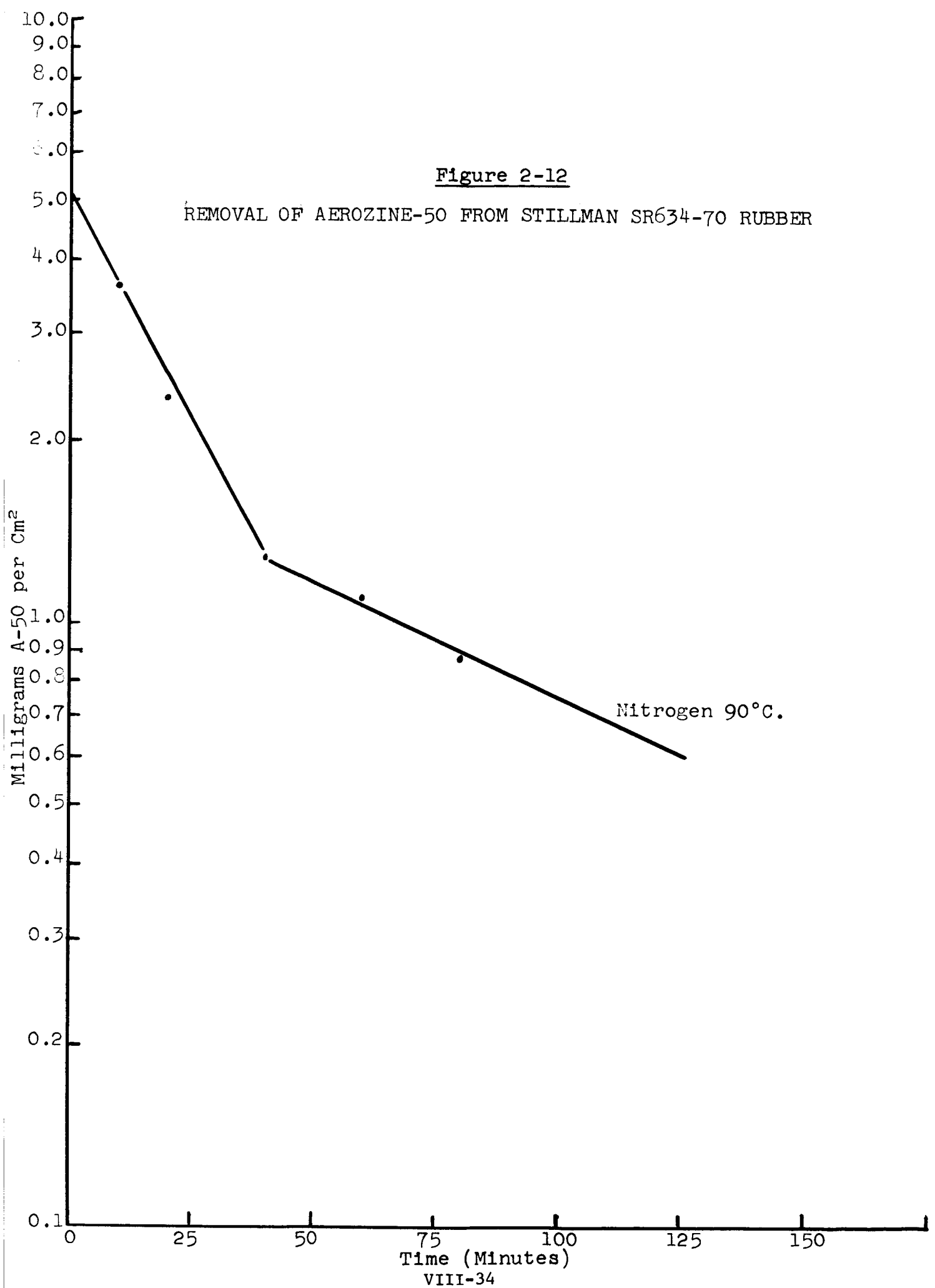


Figure 2-12

REMOVAL OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER



Aerazine-50 is a stable liquid under the extremes of heat and cold expected in storage. Upon freezing, the mixture contracts in volume. Thermal decomposition of  $N_2H_4$  begins at about 320° F; UDMH is stable up to about 700° F. The fuel blend is not shock sensitive, but the vapors are flammable over a wide range of concentrations. A mixture of these vapors with air can be detonated by a small spark. Furthermore, some metals such as copper, molybdenum, or iron oxide will catalyze decomposition at room temperature.

Studies of the liquid-vapor equilibrium have revealed no azeotropic mixtures.<sup>(29)</sup> The two components of A-50 interact endothermically on mixing. Supercooling and freezing point depressant data on  $N_2H_4$  is reported by Leonard.<sup>(18)</sup> Decomposition kinetics of  $N_2H_4$  were studied by McHale<sup>(25)</sup> who reported a simple non-chain reaction and proposes several possible mechanisms.

Tables 4-I to 4-VII and Figures 4-1 to 4-7 summarize the more important physical properties of the fuel blend and also give some of the outstanding properties of the individual components.

b. Hazards and Toxicity

The fuel blend is toxic by inhalation, ingestion, or by skin contact.

The vapors cause local irritation to the respiratory tract and to the eyes. Prolonged contact or high concentration of the fuel blend vapors cause pulmonary edema in the respiratory system. UDMH vapor is mildly irritating to the skin and eyes and will penetrate the tissue to cause systemic toxicity. In this respect, hydrazine is less dangerous but will produce an alkali-like burn or necrosis of the skin. Short exposure to the vapor results in attack on the central nervous system causing hypernea and convulsions. Longer exposure may cause death.<sup>(2)</sup> The concentrations of vapors which are hazardous to the eyes are not necessarily high enough to cause attack on other areas. Prolonged eye contact with hydrazine vapors will cause the eyes to become swollen and inflamed and can cause temporary loss of sight. In some instances, the blindness lasts for about three days, but, within a week, full recovery usually occurs.

The allowable concentration (MAC) in air of  $N_2H_4$  is 1 ppm and 0.5 ppm for UDMH for an 8-hour day.<sup>(19)</sup> Personnel suffering from over exposure to vapors should be immediately removed to an uncontaminated atmosphere and kept as quiet as possible while administering first aid.<sup>(44)</sup> Liquid hydrazine will cause permanent blindness if first aid is not rendered immediately.<sup>(12)</sup>

Patrick and Black<sup>(31)</sup> give detailed description of the pathological and toxic effects on monkeys and rats of small repeated doses of the fuel components. Weir et al<sup>(43)</sup> discussed the mechanism of acute toxic effects of UDMH. If the fuel blend should come in contact with the skin, the contaminated clothes should be removed immediately and the exposed area washed thoroughly with large quantities of water while medical attention is summoned. Eyes exposed to liquid A-50 should be immediately rinsed with clean water for 15 minutes during which time proper medical help, preferably an ophthalmologist, is summoned.

## 2. Nitrogen Tetroxide

### a. Properties and Reactions

Nitrogen tetroxide is a heavy liquid which boils near room temperature (70.07° F). The liquid is an equilibrium mixture of about 85% N<sub>2</sub>O<sub>4</sub> with 15% NO<sub>2</sub> at 68° F. The presence of the NO<sub>2</sub> gives the liquid its characteristic dark brown color, but as the temperature is lowered, the equilibrium favors less NO<sub>2</sub> and thus the solutions approach a pale yellow color.<sup>(27)</sup> N<sub>2</sub>O<sub>4</sub> is normally handled as a gas. If the N<sub>2</sub>O<sub>4</sub> falls within the specifications shown in Table 4-VIII where water content is 0.1% or less, storage in most steel containers is practicable.<sup>(30)</sup>

Nitrogen tetroxide is a very strong, corrosive oxidizing agent and extremely poisonous. It is hypergolic with UDMH, N<sub>2</sub>H<sub>4</sub>, aniline, furfuryl, alcohol, and many other combustible compounds.<sup>(1)</sup> With sufficient shock, N<sub>2</sub>O<sub>4</sub> can be detonated with certain chlorinated hydrocarbons and many other compounds not normally thought to be explosive.<sup>(23)</sup> N<sub>2</sub>O<sub>4</sub> is not sensitive to mechanical shock or heat, but above 302° F free oxygen is dissociated. On cooling, the free oxygen recombines to form N<sub>2</sub>O<sub>4</sub>. It is non-flammable but will easily support combustion.<sup>(1)</sup>

N<sub>2</sub>O<sub>4</sub> is soluble in water and reacts with water to form nitric and nitrous acids (N<sub>2</sub>O<sub>4</sub> + H<sub>2</sub>O → HNO<sub>3</sub> + HNO<sub>2</sub>). The nitrous acid undergoes further decomposition (3HNO<sub>2</sub> → HNO<sub>3</sub> + 2NO↑ + H<sub>2</sub>O). NO is sparingly soluble but may undergo oxidation (2NO + O<sub>2</sub> → 2NO<sub>2</sub>).<sup>(34)</sup> A report by Coon and Streib<sup>(13)</sup> on the dissociation of N<sub>2</sub>O<sub>4</sub> and its products indicates that the dissociation cannot be correctly calculated from pressure data at elevated temperature.

The properties of N<sub>2</sub>O<sub>4</sub> are shown in Tables 4-VIII through 4-XIV and Figures 4-8 through 4-14.



b. Hazards and Toxicity

The effects of liquid  $N_2O_4$  are similar to those of 70%  $HNO_3$ ; brief exposure causes yellowing of the skin; severe burns result from longer contact. If the liquid is splashed into the eyes, blindness is likely to occur. If taken internally, severe burns result in death.<sup>(21)</sup>

The vapor phase above liquid  $N_2O_4$  is primarily  $NO_2$ . Vapor contact with skin is less harmful than liquid for a given exposure time. The vapor will cause a stinging sensation to the exposed area. The most serious problem in handling  $N_2O_4$  is probably vapor inhalation, and it is possible for harmful concentrations to be undetected by exposed personnel. Pulmonary edema or the reduction in the ability of the lungs to carry out oxygen exchange may then occur. The lag in time for symptoms to develop may complicate the effect of pulmonary edema because exposed personnel may continue with accustomed physical exertion.<sup>(35)</sup>

The threshold limit value (MAC) is given as 5 ppm for  $NO_2$  and as 2.5 ppm for  $N_2O_4$ . Dr. Silverman<sup>(20)</sup> of the Harvard Medical School of Public Health, suggested that the MAC value can be exceeded safely by a factor of 5 for a 10-minute period. Dr. E. C. Wortz<sup>(45)</sup> also did similar work and concurred with Dr. Silverman's findings.

The initial symptoms, after exposure to  $N_2O_4$ , are irritation of the eyes and throat, cough, tightness of the chest and nausea. These first symptoms are slight but, several hours later, coughing, constriction of the chest, and very difficult breathing occurs. Cyanosis, a blue tinge to the mucous membranes of the mouth, eyelids, lips, and fingernails, may follow. A person at this stage is in great danger. Repeated exposure to the fumes may lead to ulceration of the mouth and nose and to decay of the teeth. Chronic irritation can occur to the entire respiratory tract complicated by bronchitis, bronchiectasis, or secondary pulmonary emphysema.<sup>(28)</sup>

Liquid  $N_2O_4$  spills on the skin should immediately be washed with copious quantities of water. For  $N_2O_4$  splashed into the eyes, immediate flushing with clean water is mandatory. If a choice should exist as to flushing the eyes or calling a physician, the eyes must be flushed first for at least 10 minutes, keeping the victim's eyes open. After this, call for assistance at the first opportunity but continue the eye washing. A person exposed to the vapors should be removed to an uncontaminated atmosphere and proper first aid administered.<sup>(35)</sup>

E. Propellant Storage and Handling

The high energy content and toxicity of the propellants require careful design and special precautions for storage and handling. The fuel and oxidizer must be isolated from each other and also from any incompatible substances or environment.

The fuel and oxidant are stored in closed systems under nitrogen pads. The fuel blend necessitates a pad to reduce fire and vapor explosion hazards.<sup>(28)</sup> The oxidizer requires a pad to maintain a positive pressure over the liquid to suppress the dissociation to  $\text{NO}_2$ . The  $\text{N}_2\text{O}_4$  storage system should be provided with a water sprinkler system to serve as a coolant on warm days.<sup>(35)</sup> If the propellant tanks are exposed to temperatures below freezing, a heating system may be required. The propellants contract in volume on freezing, thus eliminating expansion problems associated with water.

The vessels and connecting lines of the storage facilities should be welded where possible and should comply with the ASME Boiler and Pressure Vessel code specifications.<sup>(3)</sup> The  $\text{N}_2\text{O}_4$  vessels must withstand at least 150 psia, with rupture discs set for 75 psia, and an automatic relief valve set for a lower pressure. All vents and relief valves should pass through water scrubbers.<sup>(28)</sup>

The immediate and surrounding area of storage facilities should be free of all organics and kept as meticulously clean as possible. Cotton lint, sawdust, rags, or any other material of this nature will be spontaneously ignited by absorption of fuel vapors. The storage area should be diked in some manner to contain spills. All buildings and materials of support should be fireproof and designed for a corrosive atmosphere.<sup>(28)</sup>

All vessels and lines must be adequately grounded. Electric motors and electrical control systems should be installed under the NFPA No. 70<sup>(3)</sup> explosion-proof code to eliminate any possibility of vapor contact.

Pumps used in the system should be the self-priming type, preferably centrifugal. Any other pumps should be of a design to eliminate contamination of the propellant by moisture. The pump should be of the type needing no seal or one with a seal that is compatible with the propellant.<sup>(28)</sup>

Water outlets should be strategically located in the storage area and be of sufficient size to handle fires and spills. A wind direction marker and an evacuation signal horn are needed to aid in safe evacuation. Safety shower and eye wash baths should be conveniently located. The personnel should be thoroughly educated and familiarized with the hazards of the propellants and the problems they may create.<sup>(28)</sup> Self aid and first aid procedures must be established for all possible types of exposure.

Spills of propellants always present a very serious hazard. Decontamination of  $\text{N}_2\text{O}_4$  spills is best accomplished by a water spray. The spray knocks down the vapors and contains them along with a liquid. No advantage results from using water containing additives. Decontamination of fuel blend spills was also affected by a fine water spray. The vapors should be rapidly diluted with water spray to diminish a possible fire hazard. If a fire does develop, dry chemicals and foam are most effective as extinguishers. Water is the best material for disposing of an A-50 spill since the contaminant can be flushed down the drain and the fire hazard is considerably reduced.<sup>(36)</sup>

F. Compatibility of Propellants with Materials of Construction

The materials of construction that are satisfactory for  $N_2H_4$  service are also acceptable for UDMH.<sup>(19)</sup> Some materials such as iron, molybdenum, or copper oxides, should not be used since they catalyze the decomposition of  $N_2H_4$ . At 290° F,  $N_2H_4$  violently decomposes whereas UDMH is stable up to 700° F in the presence of the above materials. Oxides of iron, lead, magnesium, and molybdenum may cause ignition of  $N_2H_4$  vapors.

Most alloys are compatible with the fuel blend. The naturally occurring oxide surface that forms on aluminum protects it from corrosive attack. The surfaces should be carefully cleaned, after fabrication, to remove contaminants such as welding slag. Any such foreign substances contaminating the system may initiate corrosion. The aluminum alloys are highly resistant to corrosion in the pH range of A-50, and prolonged exposure does not affect the mechanical properties. Alloys such as 2014-T6, 5254-f, 6061-T6, and 356 tested at 160° F for 90 days in contact with A-50 containing up to 16%  $H_2O$  showed only a slight stain in the metal above the liquid line.<sup>(6)</sup>

Stainless steel is unaffected by A-50. However, most alloys must be acid-pickled prior to use in order to prevent stains and minor deposits. Molybdenum-bearing stainless steel alloys do not form deposits, but their use is not usually recommended.<sup>(19)</sup> Only 316, 17-4PH, and AM355 Cond-H alloys gave satisfactory results when exposed to the blend at 160° F for 90 days, showing only slight staining above the liquid line and having no deposits.<sup>(6)</sup>

Ferrous alloys can be used in systems where oxygen and moisture can be eliminated and if the temperature is maintained below 160°. However, the ferrous alloys are not recommended because the possible formation of iron oxide.<sup>(19)</sup>

Nickel alloys and certain cobalt alloys, such as Haynes Stellite 25, exhibit good resistance to the fuel at low moisture levels. Titanium alloys such as C120AV show excellent resistance to the fuel blend containing up to 16% water.

Magnesium alloys show poor resistance to corrosion. Alloys of copper show good resistance, but the possible adverse effect of their oxides limit their use.

Platings such as cadmium, silver, non-porous chromium, and nickel are satisfactory for fuel blend use. Gold-plated Berylco 25 is also satisfactory but discolors during contact.<sup>(19)</sup>

The fuel blend is a strong solvent as well as a powerful reducing agent. It will attack, dissolve, or react with many of the substances that normally constitute gaskets and seats. The soft parts must show resistance to attack and still retain a volume range of  $\pm 0$  to  $\pm 25\%$  and less than a 3% durability change. Also, the soft parts must have no effect on the propellant and show no change on visual examination.

In most instances, the preservation of sealing characteristics and resilience may be given more weight than changes in physical properties.<sup>(19)</sup>

Teflon<sup>®</sup> and Teflon<sup>®</sup> products are the most resistant to chemical attack by the fuel blend. But, in contrast to its good resistance, Teflon<sup>®</sup> as gasket material has several disadvantages. Probably the most serious of these is propellant absorption and subsequent slow degassing. This effect may appear as a slight leak around the seal or may delay decontamination of the part. Teflon<sup>®</sup> has limited reuse since it lacks resilience.<sup>(19)</sup>

Certain nylons and polyethylenes show satisfactory chemical resistance, but only for a limited time or temperature, such as 30 days or 60° F. Kel-F 300 is also restricted to use of 70 days at room temperature, or 30 days at 160° F, after which it becomes brittle.<sup>(6)</sup>

Of the elastomers, certain butyl rubbers showed the best resistance to chemical attack. Parker XB800-71 and B496-7 performed well in tests at 160° F for 30 days with less than 15% loss of tensile strength. Parco 823-70 and Precision Rubber 9257 and 9357 softened from 13 to 20% when tested at 70-80° F for 50 days. Other butyl rubbers exhibited lesser degrees of resistance to the fuel blend, but most showed especially good resistance to aging. Fluorosilicons and fluororubber generally showed poorer resistance to the fuel but better resistance to solvents and heat.<sup>(19)</sup>

The only lubricant or sealant which significantly resisted washing out was Microseal 100-1. UDMH proved to be very satisfactory for use in contact with O-rings.

Table 4-XVI illustrates the behavior of construction materials on prolonged contact with the fuel blend.

The metal for N<sub>2</sub>O<sub>4</sub> service is more limited by the water content of the oxidizer than the fuel blend.

Carbon steels, aluminums, stainless steel, nickel, and Inconel are suitable for N<sub>2</sub>O<sub>4</sub> service where the moisture content is 0.1 percent or less. Only stainless steel of the 300 series and titanium exhibit adequate corrosion resistance at high moisture content for long-term service. Metals such as brass, bronze, cadmium, copper, lead, magnesium, silver, and zinc or their alloys should be avoided for use with N<sub>2</sub>O<sub>4</sub>.<sup>(19)</sup>

Titanium and several of its alloys such as Ti 65A are satisfactory for use with N<sub>2</sub>O<sub>4</sub>.<sup>(19)</sup>

Cobalt alloys, Haynes Stellite No. 6K and 25, and certain nickel alloys are acceptable for use under anhydrous conditions. Only a few elastomers are compatible with N<sub>2</sub>O<sub>4</sub>. It can dissolve, degrade, decompose, or even completely destroy the substance. Certain components in the soft parts can be extracted, causing drastic changes

in physical properties. In fact, only one material, Teflon<sup>®</sup>, was found to resist attack sufficiently for long-term service.<sup>(19)</sup>

The inadequacies of suitable elastomers for N<sub>2</sub>O<sub>4</sub> service can be further illustrated by recent research on this problem. Work with filled Teflons<sup>®</sup> and certain polyethylene-encapsulated elastomers has been successful only for short-term exposures.<sup>(22)</sup> Gamma radiation curing techniques have been tried with several elastomers to increase their resistance.<sup>(1)</sup> Very recently, a carboxy nitroso rubber has been developed as an elastomer highly resistant to N<sub>2</sub>O<sub>4</sub>. Tests on this rubber after immersion in N<sub>2</sub>O<sub>4</sub> for 90 days at 165° F showed no change in mechanical properties.<sup>(17)</sup>

Teflons<sup>®</sup>, filled with graphite, molydisulfide, asbestos, or impregnated with Teflon<sup>®</sup> fibers, usually provide adequate services in N<sub>2</sub>O<sub>4</sub> if moisture content is less than 0.10%.<sup>(22)</sup> Both Teflon<sup>®</sup> TFE and FEP soften at higher moisture concentrations.<sup>(19)</sup> Formula 53 (polyethylene with isobutylene) shows good strength resistance but undergoes swelling of about 19%.<sup>(39)</sup>

Only three lubricants-Molykote Z, Drilube 703, and Electrofilm 66C were found to be satisfactory.<sup>(22)</sup> Water glass graphite, Reddylube 100 and 200, and N<sub>2</sub>O<sub>4</sub> sealant were satisfactory for thread sealant service.<sup>(19)</sup>

The behavior of construction materials in contact with N<sub>2</sub>O<sub>4</sub> is given in Table XVII.

#### G. Detection and Analysis

The published literature includes many articles on the detection and analysis of N<sub>2</sub>O<sub>4</sub> and the hydrazines. Detection of the presence of propellant materials is of prime interest in work areas where contamination of the atmosphere is possible. Analysis of the respective propellants for impurities such as moisture and particulate solids is important to the proper functioning of the propellant system.

##### 1. Detection

The maximum allowable concentration in the atmosphere for an 8-hour day is 0.5 ppm for the fuel blend and 5 ppm for N<sub>2</sub>O<sub>4</sub>. The atmosphere in work areas exposed to possible contamination by the propellant components must be accurately monitored for propellant vapors in order to detect immediately an increase to greater than allowable concentration.

Vapor phase chromatography has been used for detection of propellants. An instrument equipped with a 1/8-inch by 3-foot glass column packed with 15% SE oil on Gas Chrom Z at 60° was used with a flame ionization detector. Successful detection of 0.5 ppm UDMH in air was accomplished. An electron capture detector used with the vapor phase chromatograph had similar sensitivity, but reaction to atmospheric oxygen or traces of other impurities yielded less reliable results.<sup>(33)</sup>

A very simple and inexpensive method for atmospheric detection of fuel vapor down to 0.5 ppm has been used. This method is colorimetric in nature and uses paradimethyl aminobenzaldehyde absorbed on paper as the coloring agent. Measured volumes of air are pumped through the paper. If fuel vapors are present in the air, the paper will turn yellow. The degree of color can be matched against standards and concentrations down to 0.5 ppm can be determined. This method has the limitation that concentrations of chlorine above 5 ppm and ammonia above 50 ppm interfere.<sup>(37)</sup>

More sophisticated detection instruments are available for air contaminants. The M.S.A. Billion-Aire instrument manufacturers claim detection down to the ppb range. It uses a relatively complex ionization chamber in which the contaminant is reacted to form a solid. This reaction constitutes a sensitization whereby the desired physical changes are correlated to concentration levels. Hydrazine is detected in the 0-50 ppb range, UDMH in the low ppm, and  $\text{NO}_2$  in the 0-10 ppm range according to claims by the manufacturer.<sup>(38)</sup>

Other means of detection utilize air contaminant impingement on chemically treated tapes or into liquid scrubbing solutions. This type of detection departs from rapid, simple atmospheric monitoring in that the information read-out occurs after analysis by conventional methods.

## 2. Analysis

Simple methods may be needed to determine the purity of the propellants. Weight percent  $\text{N}_2\text{O}_4$  can be determined in the following manner:

A 1.5 gram sample of  $\text{N}_2\text{O}_4$  is carefully collected in a sealed tube and accurately weighed. One hundred milliliters of 3%  $\text{H}_2\text{O}_2$  are added to a 500-milliliter flask in a nitrogen atmosphere. The sealed ampoule of  $\text{N}_2\text{O}_4$  is carefully inserted into the flask and broken below the liquid surface. The solution is diluted to 240 milliliters and chilled to freezing with constant shaking, then allowed to come to room temperature. The solution is next titrated with 0.5 N NaOH along with a blank, and appropriate calculation made.<sup>(10)</sup>

The nitrosyl chloride content of the  $\text{N}_2\text{O}_4$  can also be simply determined.

A portion of the 250-milliliter solution prepared as mentioned above is titrated for chloride ion by the standard  $\text{AgNO}_3$  titration method.

A non-volatile ash determination can be made as follows:

A weighed sample collected in the manner described above is placed in a prepared 100-milliliter platinum evaporating dish.

After evaporation, the dish is heated in a muffle furnace for 30 minutes at 2,000° F. The dish is cooled, desiccated, carefully reweighed, and the percent non-volatile ash is calculated.<sup>(10)</sup>

The composition of the fuel blend can also be determined:

A difference in reaction rates for acetylation of hydrazines can be used to determine the weight percent of the constituent in the blend. Acetylation of hydrazine occurs very rapidly while the UDMH reaction proceeds slowly. Two titrations are made. The first determines the total basicity of  $N_2H_4$ . The second measures UDMH after  $N_2H_4$  has reacted with acetic anhydride. The amount of water and impurities can be determined by subtracting the sum of these two values from 100.<sup>(10)</sup>

Gas chromatography is the most convenient method for analysis of water content present in the range of specification given for fuel blend.

A column of Fluoropak-80 coated with 20% Ucon Oil 550X gave very reproducible results. Water content in hydrazine in concentrations from 0.5 to 2.0 weight percent was accurately determined.<sup>(15)</sup>

The Karl Fisher method of water detection is accurate to very low concentrations. However, this method cannot be applied to detection of water in the oxidizer.<sup>(10)</sup>

To determine moisture content in a propellant tank after cleaning, an instrument such as the dew-pointer can be used. This instrument is valuable in detecting trace amounts of moisture and other vapor contaminants.

For the detection of particulate matter, various filters can be used to entrap the matter. The size and number per unit area can be determined by microscopic examination or the total level may be determined by weight gain during passage of a measured volume of gas. Elaborate electronic counting instruments are also available to quickly obtain the same information.

Many other methods of analysis are readily available in the published literature. A useful catalog of infrared spectra covering rocket fuels and products of combustion in vapor and liquid combination has been prepared. This type of analysis is useful in any application where a wide variety of products are to be identified and measured.<sup>(32)</sup>

H. Tables

TABLE 4-I

PROPELLANT SPECIFICATION - 50/50 FUEL BLEND\*

<u>Chemical Requirements</u>	<u>Specification (Wt. %)</u>
UDMH	47.0 (min.)
N <sub>2</sub> H <sub>4</sub>	51.0 ± 0.8
Total N <sub>2</sub> H <sub>4</sub> and UDMH	98.2 (min.)
H <sub>2</sub> O and Other Soluble Impurities	1.8 (max.)

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(Reference 7)

\*The above specifications define the fuel Aerozine-50 and apply in all instances of reference.



TABLE 4-II  
PHYSICAL PROPERTIES

50/50 Fuel Blend

Molecular Weight (Avg.) - - - - -	45.0
Melting Point* - - - - -	18.8°F.
Boiling Point - - - - -	158.2°F.
Physical State - - - - -	Colorless Liquid
Density of Liquid at 77°F. - - -	56.1 lb./ft. <sup>3</sup>
Viscosity of Liquid at 77°F. - -	54.9 x 10 <sup>-5</sup> lb./ft-sec.
Vapor Pressure at 77°F. - - - -	2.75 psia.
Critical Temperature (calc.) - -	634°F.
Critical Pressure (calc.) - - - -	1696 psia.
Heat of Vaporization (calc.) - -	425.8 BTU/lb.
Heat of Formation at 77°F. (calc.)	527.6 BTU/lb.
Specific Heat at 77°F. (calc.) -	0.694 BTU/lb-°F.
Thermal Conductivity at 77°F. - -	
(calc.) - - - - -	0.151 BTU/ft-hr-°F.

(Reference 1)

Hydrazine

Molecular Weight - - - - -	32
Melting Point - - - - -	35°F.
Boiling Point - - - - -	236°F.
Density at 68°F. - - - - -	8.48 lb/gal.
Critical Pressure - - - - -	2120 psig.
Critical Temperature - - - - -	716°F.
Flash Point (open cup) - - - - -	100-126°F.

(Reference 9)

Unsymmetrical Dimethyl Hydrazine

Molecular Weight - - - - -	60
Melting Point - - - - -	71°F.
Boiling Point - - - - -	146°F.
Density at 68°F. - - - - -	6.6 lb/gal.
Critical Temperature - - - - -	480°F.
Critical Pressure - - - - -	865 psig.
Flash Point (closed cup) - - - -	3°F.

(Reference 9)

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\*Mixtures complying to specifications in Table 4-I.

TABLE 4-III

## DISTILLATION RANGE OF THE 50/50 FUEL BLEND

<u>Blend Composition by Weight %</u>		
UDMH	48.7	
N <sub>2</sub> H <sub>4</sub>	50.4	
H <sub>2</sub> O + impurities	0.9	

<u>Temperature</u> (°F)	<u>Volume %</u> (Distilled)	<u>Distillate Analyses*</u>
149.0	First Drop Distilled	-
158.0	10	86.0% UDMH, 8.0% N <sub>2</sub> H <sub>4</sub>
161.6	20	85.0% UDMH, 9.0% N <sub>2</sub> H <sub>4</sub>
167.0	30	-
170.6	40	-
194.0	50	79.0% UDMH, 15.0% N <sub>2</sub> H <sub>4</sub>
233.6	60	-
235.4	70	-
235.4	80	100% N <sub>2</sub> H <sub>4</sub>
239.0	90	95% N <sub>2</sub> H <sub>4</sub>

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(Reference 6)

\*Analysis done spectrally with calibration curves for UDMH and N<sub>2</sub>H<sub>4</sub> concentration range of 45 to 55% by weight.

TABLE 4-IV

VAPOR PRESSURE OF 50/50 FUEL BLEND AT 46% ULLAGE

<u>Temperature</u> (°F)	<u>Vapor Pressure</u> (Psia)	<u>Reference</u> No.
14.0	0.55	1
23.0	0.71	1
32.0	0.92	1
68.0	2.09	1
77.0	2.75	1
85.3	3.08	7
86.0	3.42	1
104.0	5.00	1
108.9	5.30	7
122.0	7.30	1
135.3	9.29	7
140.0	10.50	1
159.8	15.10	1

TABLE 4-V

## SOLUBILITY OF VARIOUS GASES IN 50/50 FUEL BLEND

<u>Pressurizing Gas</u>	<u>Temperature (°F)</u>	<u>Solubility (Wt %)</u>	<u>Final Gas Pressure (Psia)</u>
Nitrogen	70.0	<0.01	86.0
	32.0	<0.01	79.4
Helium	71.5	0.012 ± 0.008	63.6
	33.0	<0.008	60.7
Ammonia	57.5	0.26 ± 0.01	38.0
	70.0	0.25 ± 0.01	44.4

---

(References 6 and 8)

TABLE 4-VI

## HEAT CAPACITY OF 50/50 FUEL BLEND

(Calculated by Aerojet-General)

<u>Temperature (°F)</u>	<u>Heat Capacity (BTU/Lb-°F)</u>
21	0.680
35	0.684
63	0.692
81	0.696
99	0.702
135	0.709
153	0.715
250	0.743
350	0.780
420	0.814

---

(Reference 7)

TABLE 4-VII

FLASH AND FIRE POINTS OF 50/50 FUEL BLEND  
WITH VARIOUS WATER DILUTIONS

(Using a Modified Cleveland Open-Cup Tester)

<u>H<sub>2</sub>O in Fuel Blend (Vol. %)</u>	<u>Flash Point (°F.)</u>	<u>Fire Point (°F.)</u>
Undiluted	38	38
10	40	40
20	35	35
50	110	125
60	160	160
65	180	200
75	>212	>212

TABLE 4-VIII  
PROPELLANT SPECIFICATION\* -  $\text{N}_2\text{O}_4$

<u>Chemical Requirements</u>	<u>Specification (Wt. %)</u>
$\text{N}_2\text{O}_4$ Assay	99.5 (min)
$\text{H}_2\text{O}$ Equivalent	0.1 (max)
Chloride as $\text{NOCl}$	0.06 (max)
Non-Volatile Ash	0.01 (max)

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\*Taken from Mil-P-26539 specifications (USAF) 18 July 1960

TABLE 4-IX  
PHYSICAL PROPERTIES OF N<sub>2</sub>O<sub>4</sub>

Empirical Formula	N <sub>2</sub> O <sub>4</sub> ⇌ 2NO <sub>2</sub>
Structural Formula	$  \begin{array}{c}  \text{O} \quad \quad \text{O} \\  \diagdown \quad \diagup \\  \text{N} - \text{N} \\  \diagup \quad \diagdown \\  \text{O} \quad \quad \text{O}  \end{array}  $
Molecular Weight	92.016
Physical State	Red-brown liquid
Melting Point	11.84°F.
Boiling Point	70.07°F.
Heat Formation at 77°F. (Liquid)	-87.62 BTU/lb.
Vapor Pressure at 77°F.	17.7 psia.
Viscosity at 77°F.	0.0002796 lb/ft-sec. 0.410 centipoise
Density at 77°F.	89.34 lb/ft <sup>3</sup>
Heat Capacity at 70°F.	0.370 BTU/lb-°F.
Critical Temperature	316.8°F.
Critical Pressure	1469 psia.
Thermal Conductivity at 40°F. and 200 psia.	0.0812 BTU/ft-hr-°F.
Heat Vaporization	178 BTU/lb.
Heat of Fusion	68.4 BTU/lb.
(Reference 27)	

TABLE 4-X  
EQUILIBRIUM VALUES - PERCENT DISSOCIATION OF  $N_2O_4$   
 $N_2O_4 \rightleftharpoons 2NO_2$

Temperature (°F)	Pressure (psia)		
	<u>7.4</u>	<u>14.7</u>	<u>29.4</u>
68	19.5	15.8	7.2
104	38.7	31.0	15.1
140	66.0	50.4	28.2
176	85.0	73.8	46.7
212	93.7	88.0	66.5

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(Reference 27)



TABLE 4-XI  
VAPOR PRESSURE OF N<sub>2</sub>O<sub>4</sub>

<u>Temperature (°F)</u>	<u>Vapor Pressure (psia)</u>	<u>Temperature (°F)</u>	<u>Vapor Pressure (psia)</u>
11.8	2.70	180	163.29
14	2.90	190	196.35
32	5.08	200	235.01
50	8.56	210	281.56
68	13.92	220	332.8
70	14.78	230	393.2
80	18.98	240	463.3
90	24.21	250	543.9
100	30.69	260	636.3
110	38.62	270	732.6
120	48.24	280	864.1
130	59.98	290	1000.5
140	74.12	300	1160.1
150	91.06	310	1336.5 <sup>a</sup>
160	111.24	316.8 <sup>b</sup>	1469.0 <sup>a</sup>
170	135.14		

a - Value extrapolated.

b - Critical pressure estimated from measured critical temperature.

(References 1 and 27)

TABLE 4-XII  
DENSITY OF LIQUID N<sub>2</sub>O<sub>4</sub>  
(Under its Own Vapor Pressure)

Temperature (°F)	Specific Gravity	Density	
		(lb/ft <sup>3</sup> )	(lb/gal)
11.8	1.515	94.54	12.62
32.0	1.490	93.05	12.44
50.0	1.470	91.77	12.27
68.0	1.447	90.34	12.08
77.0	1.431	89.34	11.94
95.0	1.412	88.15	11.76
104.0	1.400	87.40	11.66
113.0	1.388	86.61	11.56
118.4	1.379	86.05	11.49
122.0	1.375	85.80	11.45
129.2	1.363	85.05	11.35

---

(References 1 and 27)

TABLE 4-XIII  
VISCOSITY OF N<sub>2</sub>O<sub>4</sub> IN THE LIQUID PHASE

		<u>Temperature (°F)</u>								
		40	70	100	130	160	190	220	250	280
		<u>Bubble Pressure (psia)</u>								
			14.8	30.7	60.0	111.2	196.4	332.8	543.9	864.1
<u>Pressure (psia)</u>		<u>Viscosity (centipoise)</u>								
Bubble Point		0.4990	0.4132	0.3420	0.2784	0.2235	0.1752	0.1325	0.0924	0.0570
200		0.5021	0.4155	0.3441	0.2800	0.2250	0.1753			
400		0.5055	0.4180	0.3470	0.2820	0.2281	0.1804	0.1350		
600		0.5090	0.4208	0.3495	0.2840	0.2310	0.1850	0.1420	0.0943	
800		0.5121	0.4232	0.3520	0.2861	0.2334	0.1896	0.1482	0.1028	
1000		0.5150	0.4260	0.3544	0.2880	0.2355	0.1939	0.1539	0.1100	0.0630
1250		0.5190	0.4297	0.3566	0.2906	0.2380	0.1975	0.1599	0.1179	0.0713
1500		0.5230	0.4330	0.3587	0.2913	0.2400	0.2010	0.1646	0.1252	0.0798
1750		0.5270	0.4366	0.3608	0.2949	0.2420	0.2040	0.1686	0.1319	0.0881
2000		0.5310	0.4400	0.3628	0.2965	0.2440	0.2083	0.1720	0.1370	0.0940
2200		0.5345	0.4433	0.3649	0.2990	0.2459	0.2060	0.1742	0.1400	0.0990
2500		0.5382	0.4470	0.3670	0.3010	0.2480	0.2098	0.1764	0.1430	0.1045
2750		0.5422	0.4502	0.3691	0.3024	0.2496	0.2110	0.1785	0.1444	0.1090
3000		0.5465	0.4535	0.3713	0.3042	0.2510	0.2127	0.1800	0.1470	0.1126
3500			0.4593	0.3753	0.2070	0.2540	0.2151	0.1822	0.1510	0.1170
4000			0.4655	0.3792	0.3095	0.2568	0.2183	0.1850	0.1532	0.1210
4500			0.4714	0.3830	0.3118	0.2600	0.2200	0.1880	0.1555	0.1249
5000			0.4782	0.3869	0.3145	0.2625	0.2229	0.1900	0.1579	0.1280

TABLE 4-XIV  
HEAT CAPACITY OF LIQUID  $\text{N}_2\text{O}_4$

<u>Temperature</u> <u>(°F)</u>	<u>Heat Capacity</u> <u>(BTU/Lb.-°F.)</u>
20.5	0.3564
27.0	0.3578
36.1	0.3598
45.6	0.3624
56.8	0.3652
64.8	0.3667

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(Reference 14)

TABLE 4-XV  
SOLUBILITY OF NITROGEN AND HELIUM  
IN LIQUID  $\text{N}_2\text{O}_4$

<u>Pressurizing Gas</u>	<u>Temperature (°F)</u>	<u>Solubility (Wt.%)</u>	<u>Final Gas Pressure (psia)</u>
Nitrogen	70	0.20±0.01	63.7
	32	0.14±0.01	64.2
Helium	73	0.04±0.01	54.3
	32	0.02±0.01	55.4

---

(Reference 8)

TABLE 4-XVI

COMPATIBILITY OF CONSTRUCTION MATERIALS  
WITH 50/50 FUEL BLEND

<u>Material</u>	<u>Temp. (°F.)</u>	<u>Exposure Time</u>	<u>Remarks</u>
Birch Wood	75	2 hr 30 min	Wood grain split
Concrete			
Bare	75	13 hr	No visual effect
Coated w/water glass	75	1 hr 30 min	Water glass crystallized and powdered off
Coated w/water glass and floor enamel (Esco Brand 41138)	75	1 hr 15 min	Paint blistered
Coated w/water glass and Chex-Wear floor enamel	75	6 min	Paint blistered
Coated with Rockflux	75	10 hr 30 min	No visual effect
Mild Steel Coated With			
Tygon K Paint	75	1 hr	Paint blistered
Catalac improved paint	75	1 hr 30 min	Grainy appearance; lifted when totally immersed
Co-polymer P-200G	75	3 min	Paint was removed
Sauereisen 47 (4 coatings)	75	7 hr	First coating was removed in 1 hr; blistered but did not penetrate 4 coatings.
CA 9747 Primer Paint	75	10 min	Blistered and dis-colored
Corrosite Clear 581	75	1 hr 15 min	Blistered

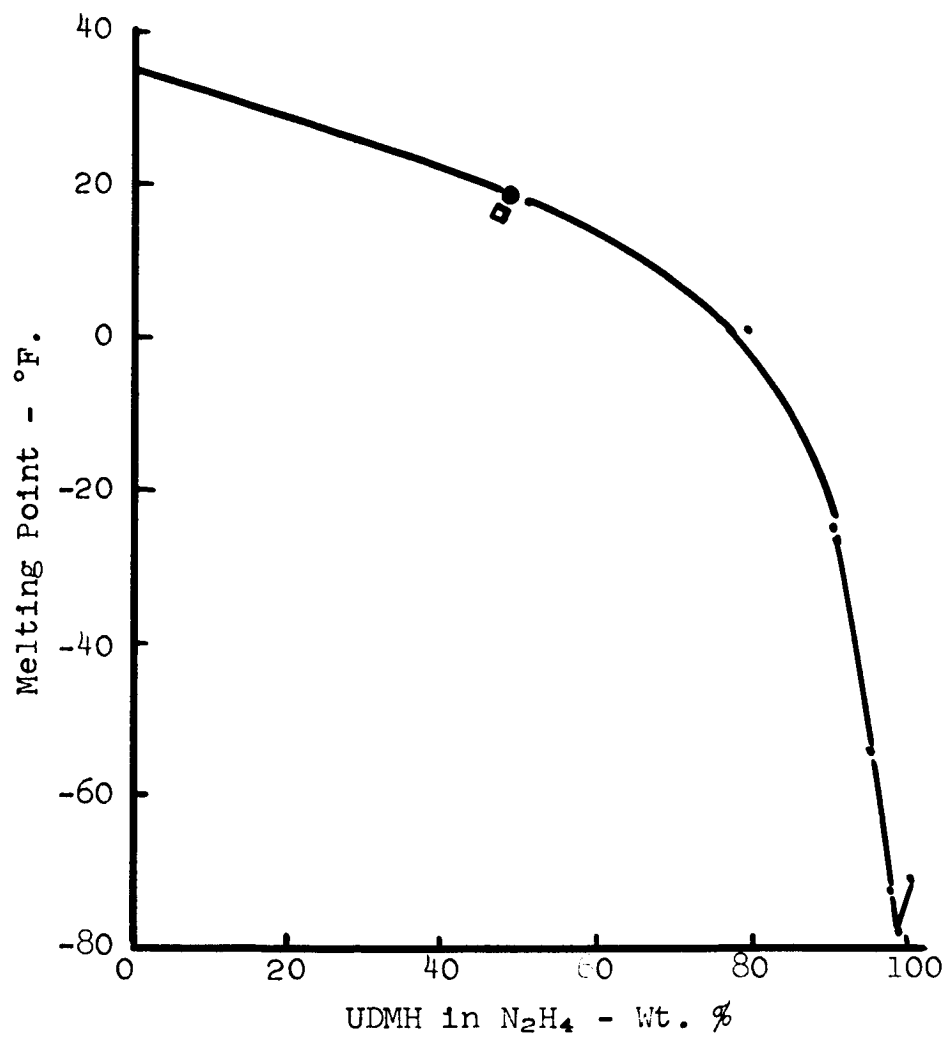
TABLE 4-XVII  
COMPATIBILITY OF CONSTRUCTION MATERIALS WITH  $N_2O_4$

<u>Material</u>	<u>Temp. (°F.)</u>	<u>Exposure Time</u>	<u>Remarks</u>
Birch Wood	75	30 min	Surface darkened; attacked at $H_2O-N_2O_4$ interface
Concrete			
Bare	75	1 hr 42 min	Concrete attacked
Coated w/water glass	75	1 hr	No apparent reaction; affords protection
Coated w/water glass and floor enamel (Esco Brand 41138)	75	30 min	Reaction at $H_2O-N_2O_4$ interface after 6 minutes; stripped to water glass.
Coated w/water glass and Chex-Wear floor enamel	75	3 min	Only paint removed
Coated w/Rockflux	75	1 hr 15 min	$N_2O_4$ absorbed; adhesion weakened; material turned white.
Mild Steel Coated with			
Tygon K paint	75	20 min	Paint blistered
Catalac, improved	75	10 min	Paint blistered; lifted when totally immersed
Copolymer P-200G	75	2 min	Dissolved immediately
Sauereisen 47 (4 coatings)	75	10 min	Dissolved
CA9747 Primer Paint	75	2 min	Reaction and dis- colored immediately
Corrosite Clear 581	75	30 min	Blistered

I. Figures

Figure 4-1

MELTING POINT OF AEROZINE-50

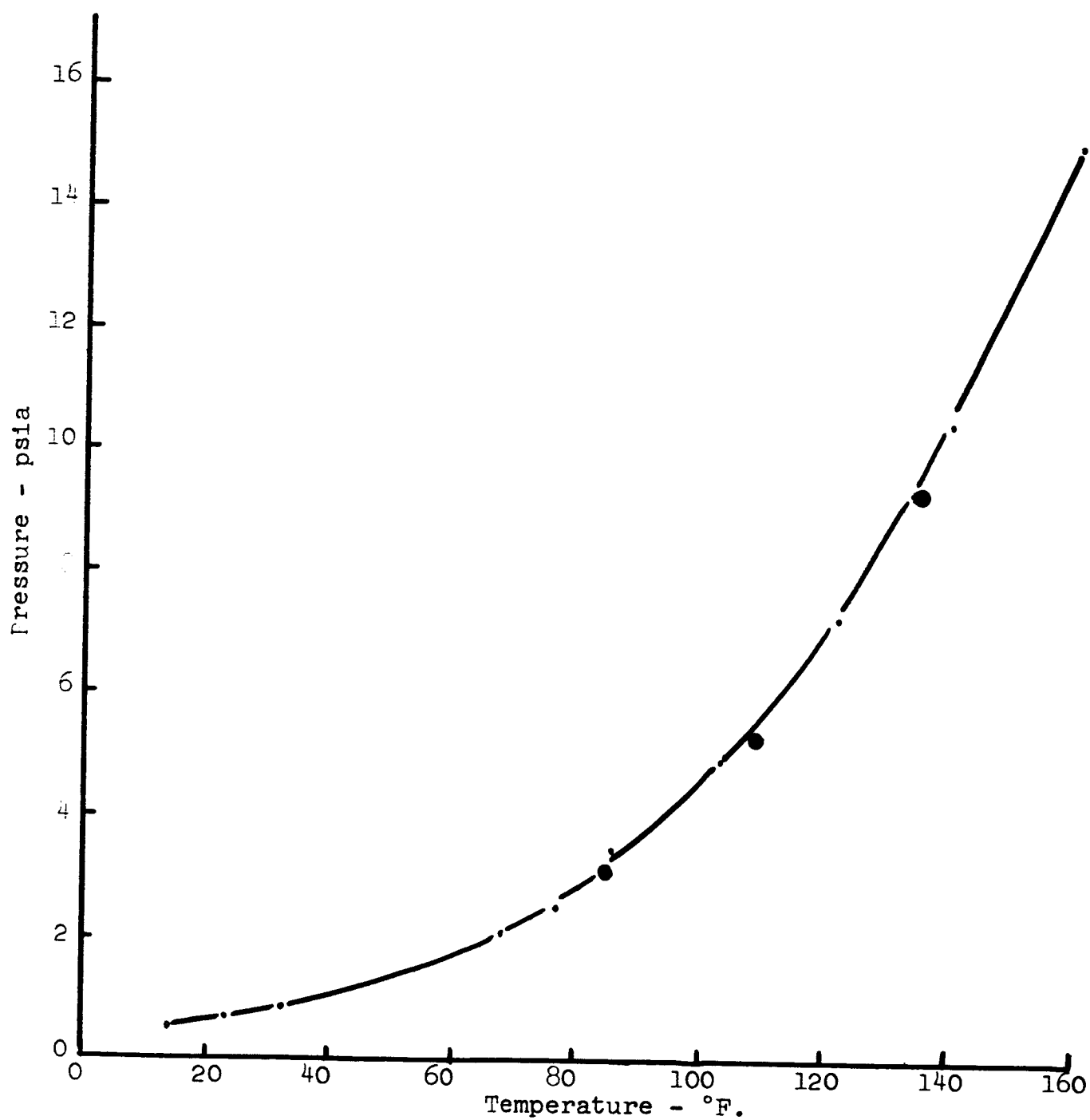


(Reference 7)



Figure 4-2

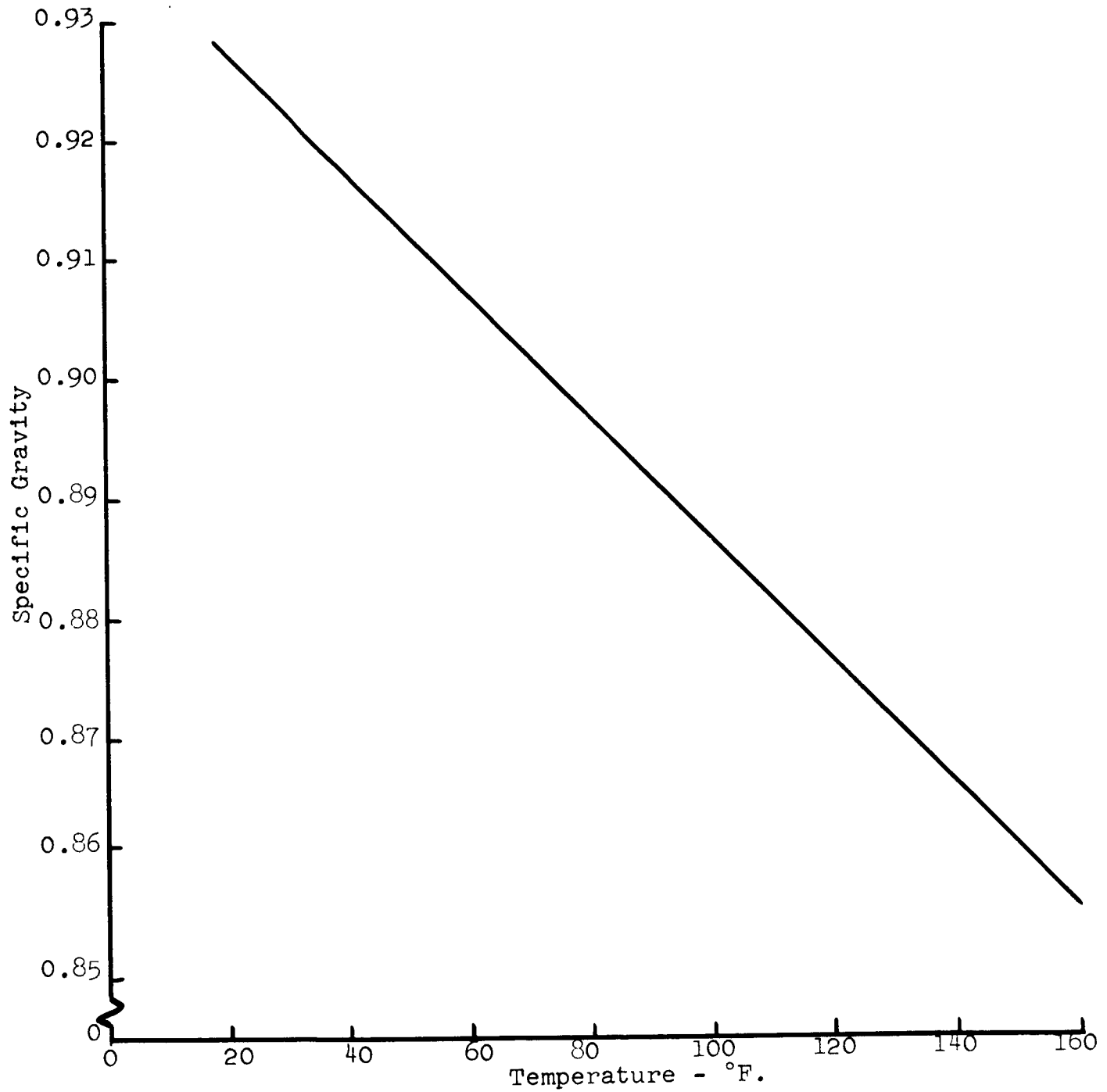
VAPOR PRESSURE OF AEROZINE-50



(Reference 7)

Figure 4-3

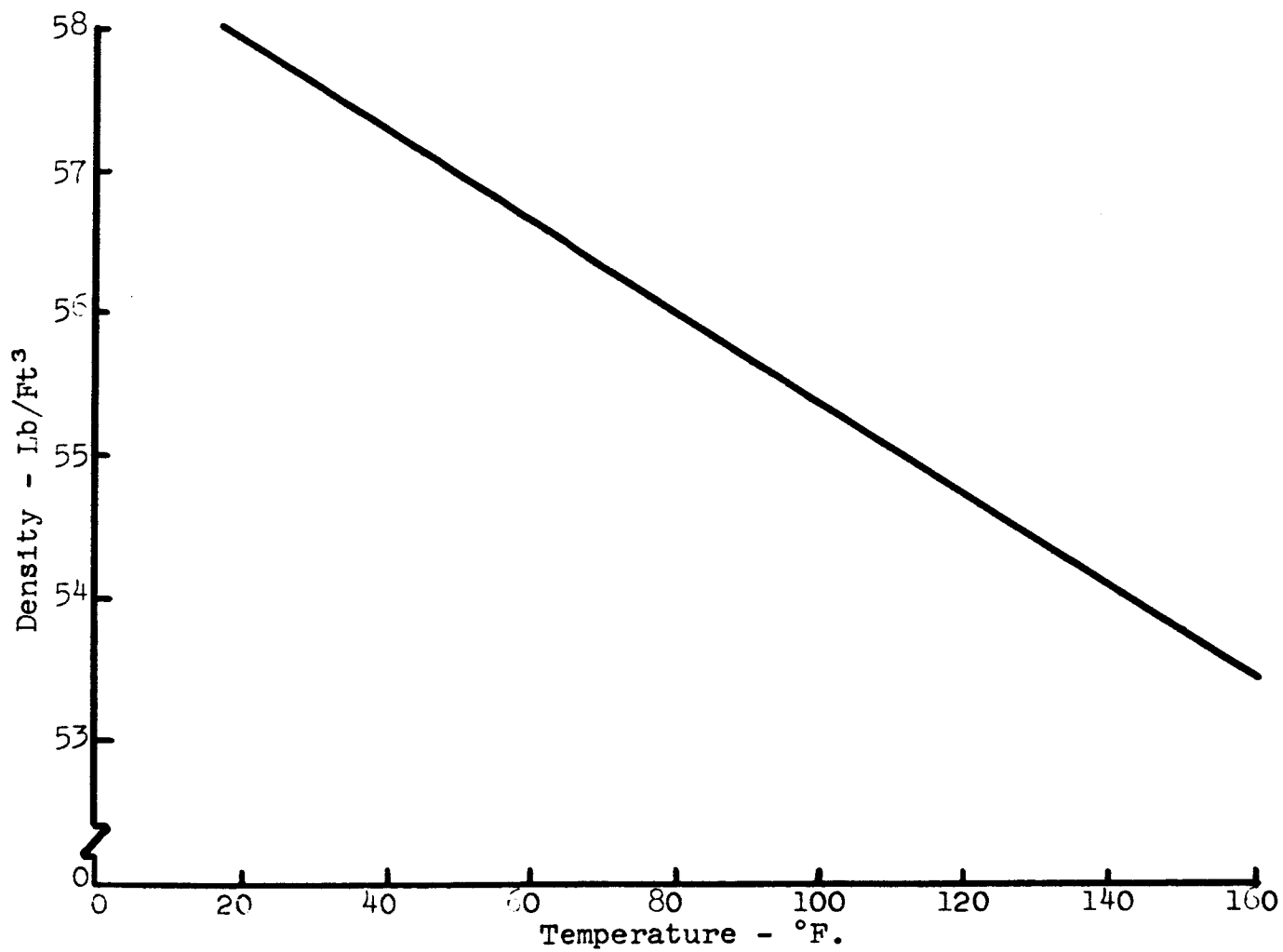
SPECIFIC GRAVITY OF AEROZINE-50



(Reference 1)

Figure 4-4

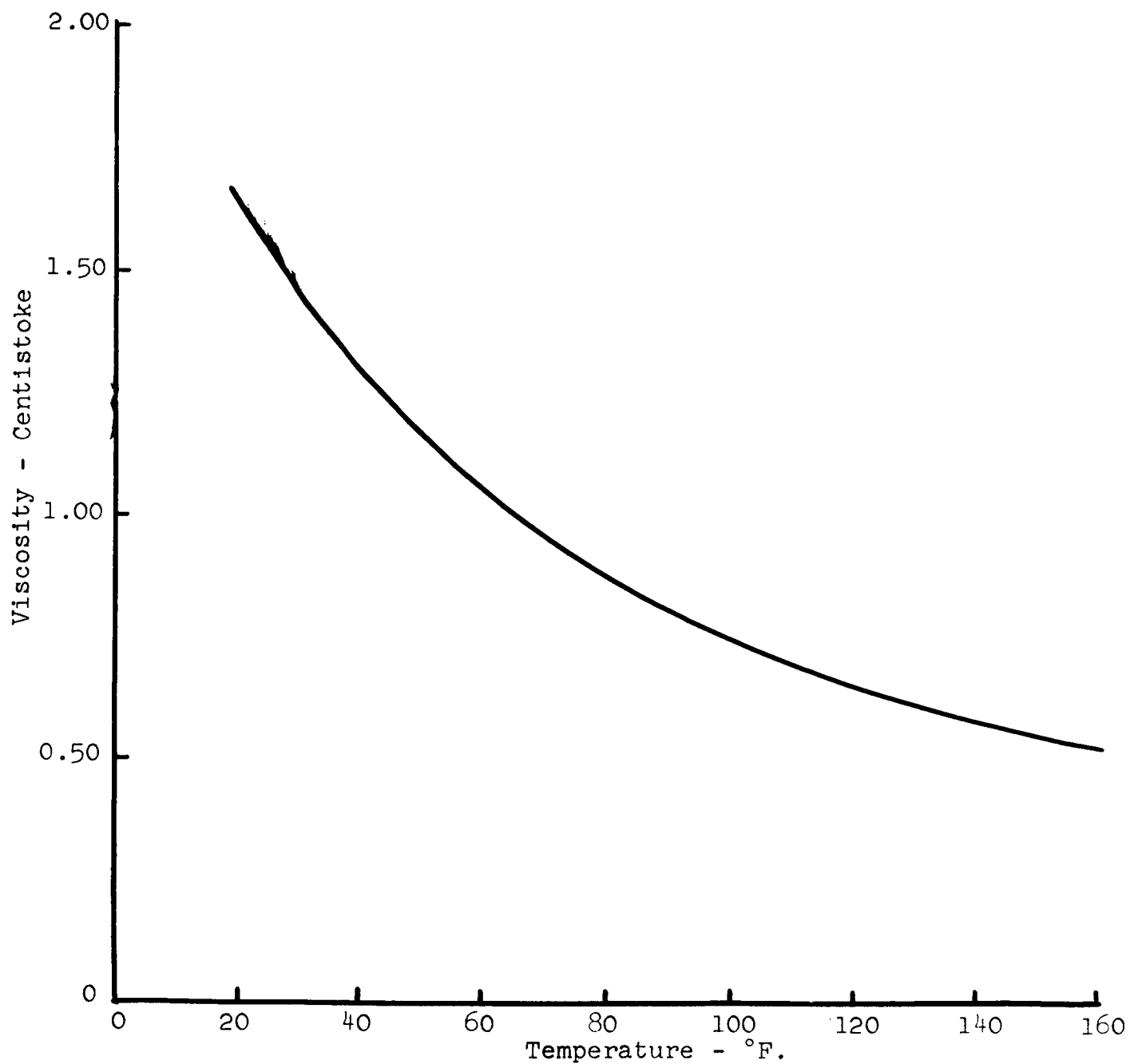
DENSITY OF AEROZINE-50



(Reference 1)

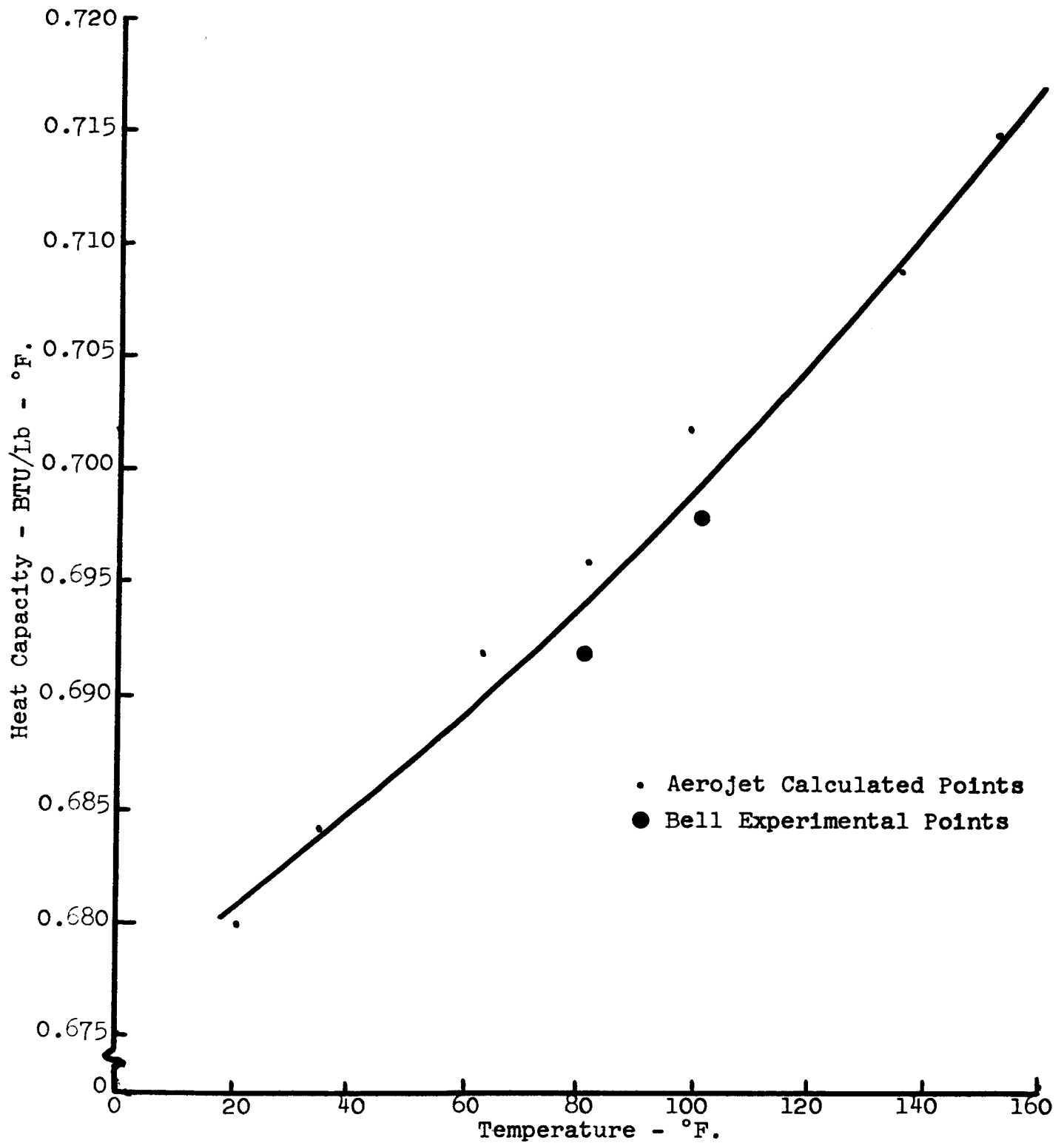
Figure 4-5

VISCOSITY OF AEROZINE-50



(Reference 1)

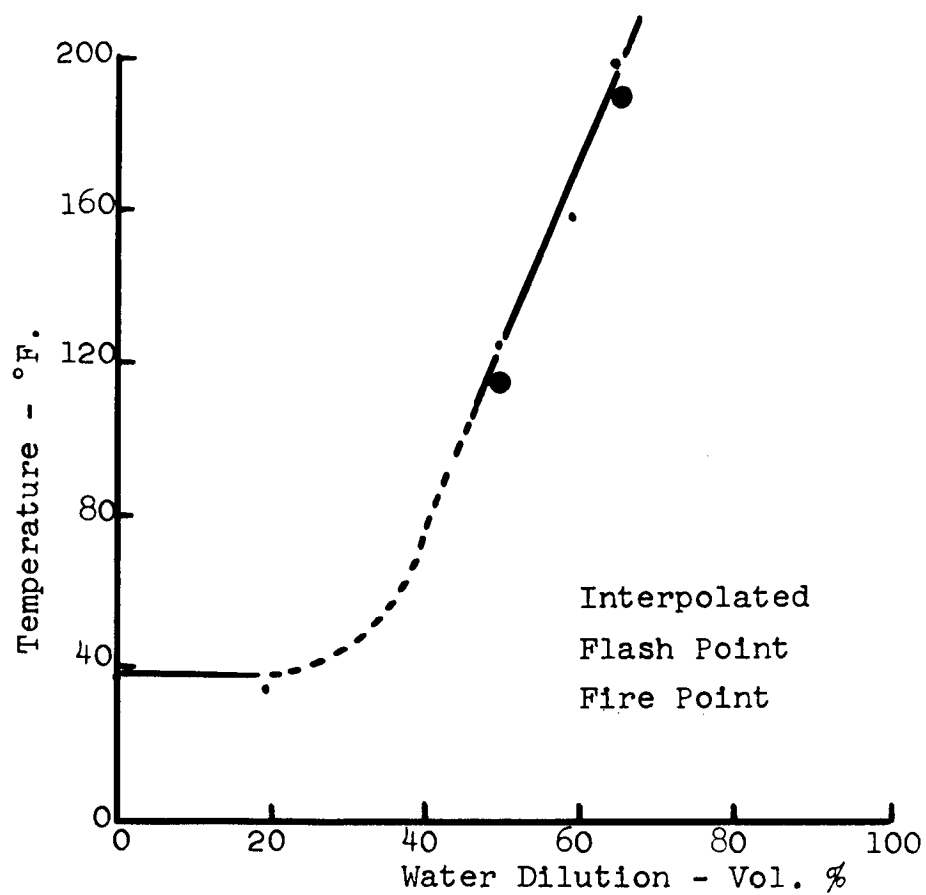
Figure 4-6  
HEAT CAPACITY OF AEROZINE-50



(References 1 and 6)

Figure 4-7

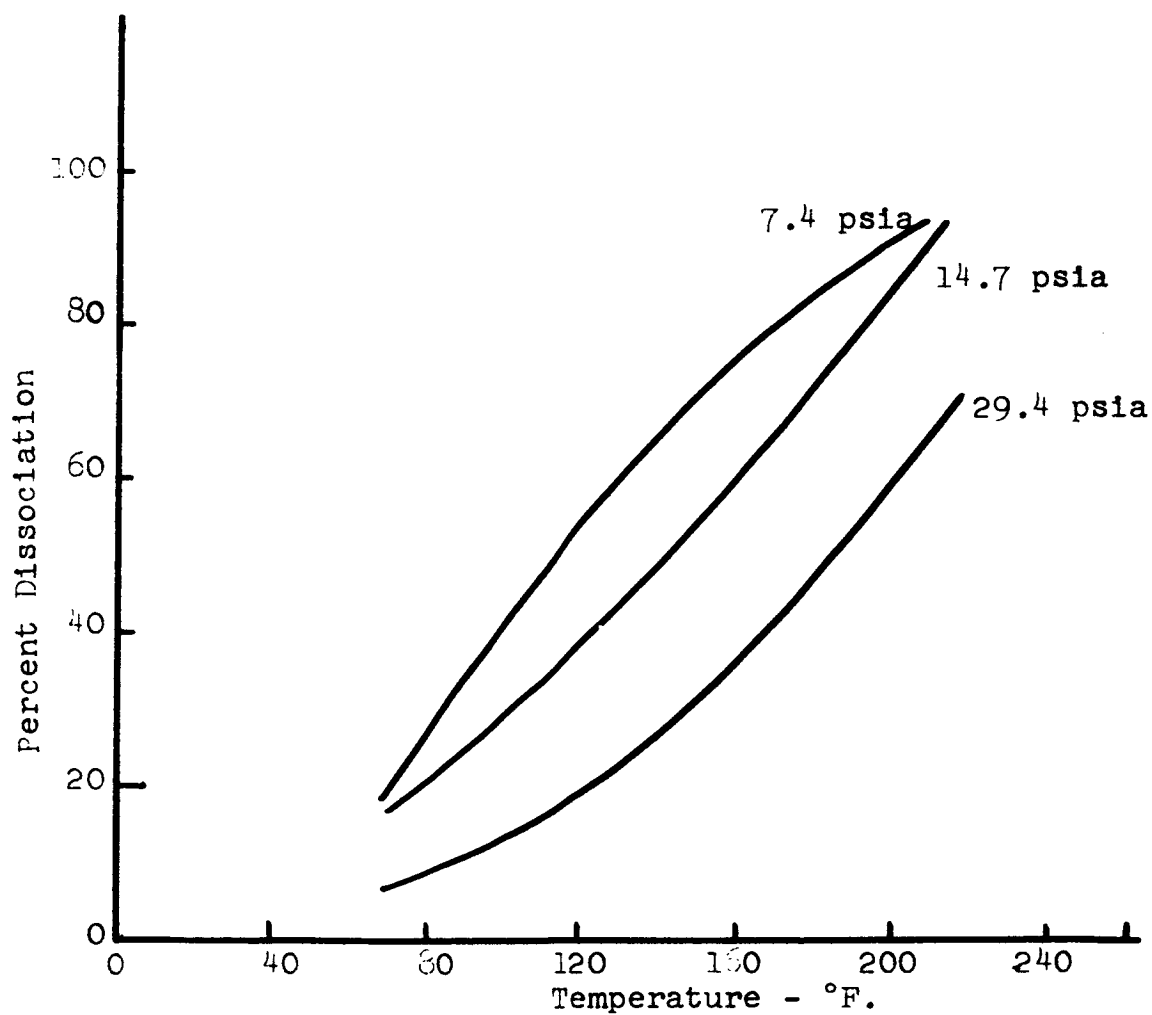
FLASH AND FIRE POINTS OF AEROZINE-50  
WITH VARIOUS WATER DILUTIONS



(Reference 8)

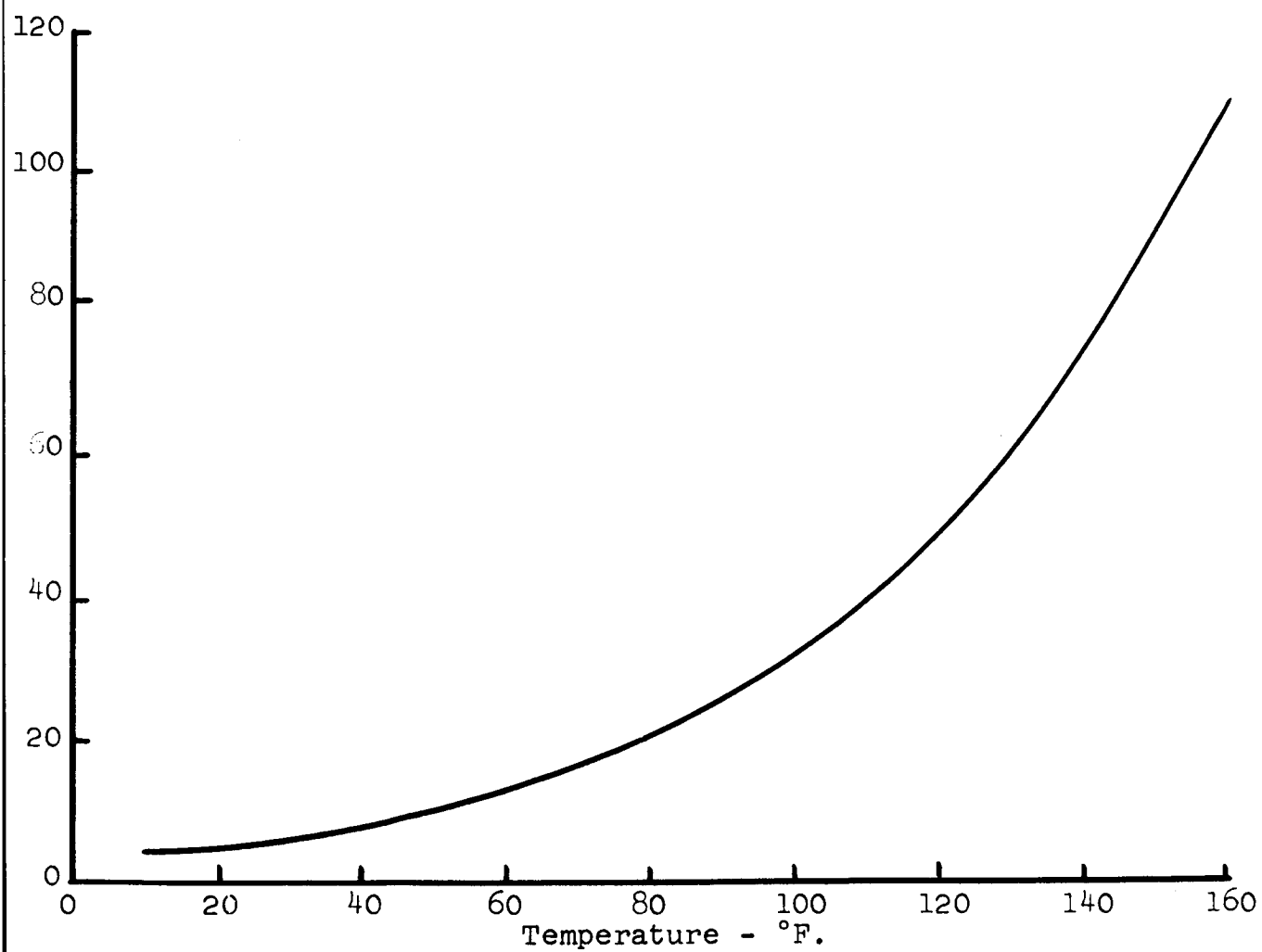
Figure 4-8

EQUILIBRIUM VALUES  
DISSOCIATION OF  $\text{N}_2\text{O}_4$



(Reference 7)

Figure 4-9  
VAPOR PRESSURE OF  $\text{N}_2\text{O}_4$

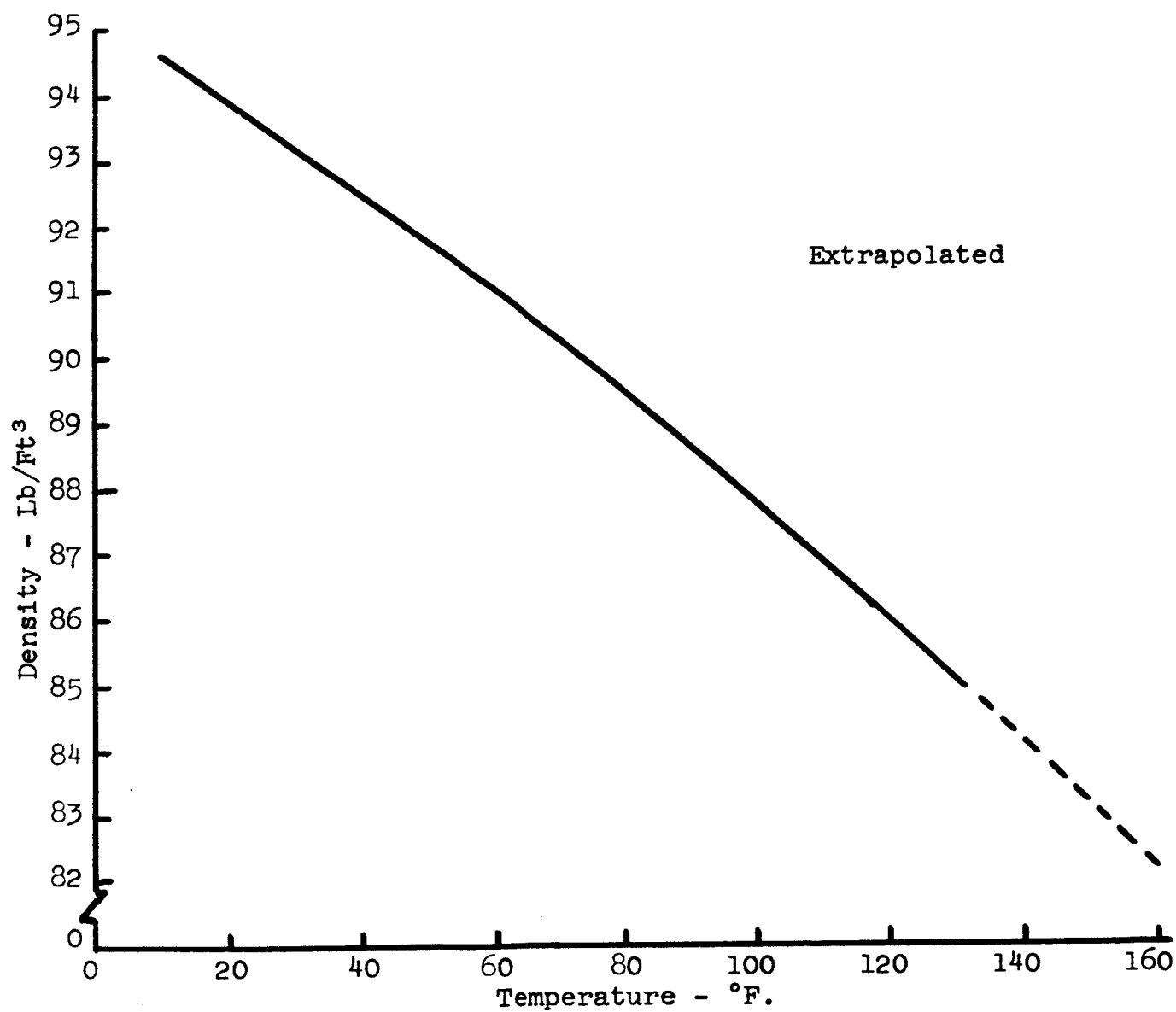


(References 1 and 3)



Figure 4-10

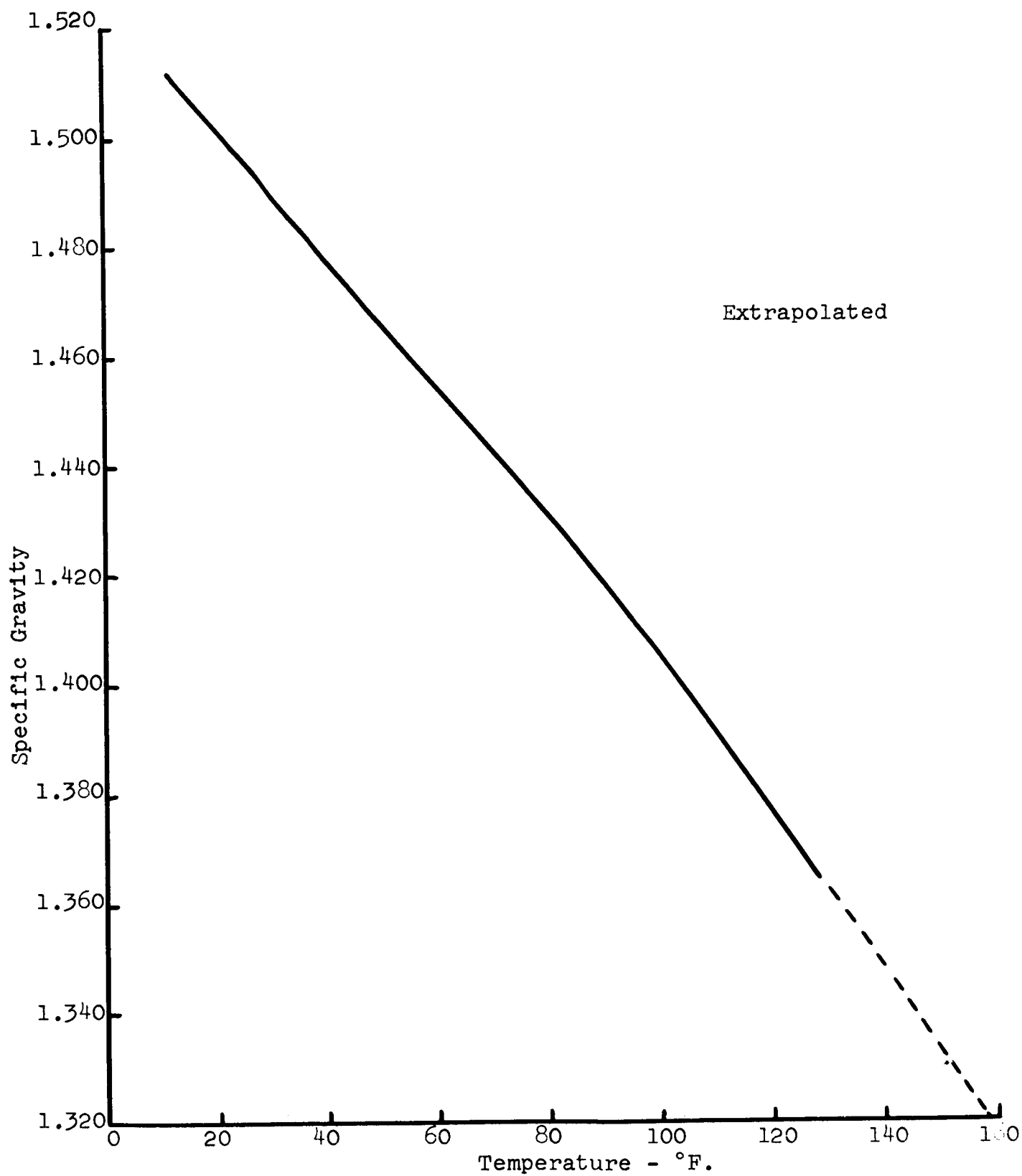
DENSITY OF  $N_2O_4$  UNDER ITS OWN VAPOR PRESSURE



(References 1 and 3)

Figure 4-11

SPECIFIC GRAVITY OF  $N_2O_4$  UNDER ITS OWN VAPOR PRESSURE



(References 1 and 3)

Figure 4-12

EFFECTS OF TEMPERATURE ON VISCOSITY  
IN THE LIQUID PHASE,  $N_2O_4$

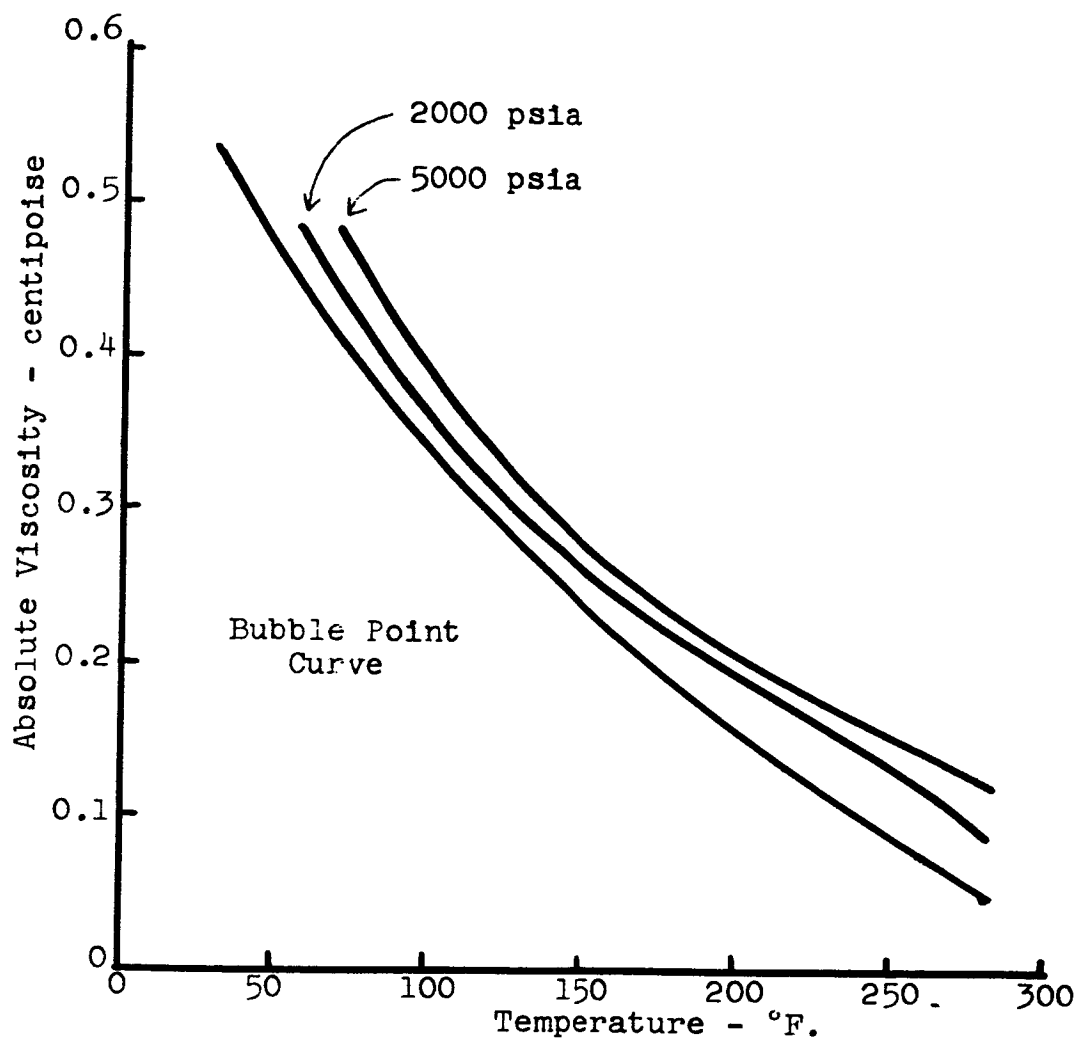
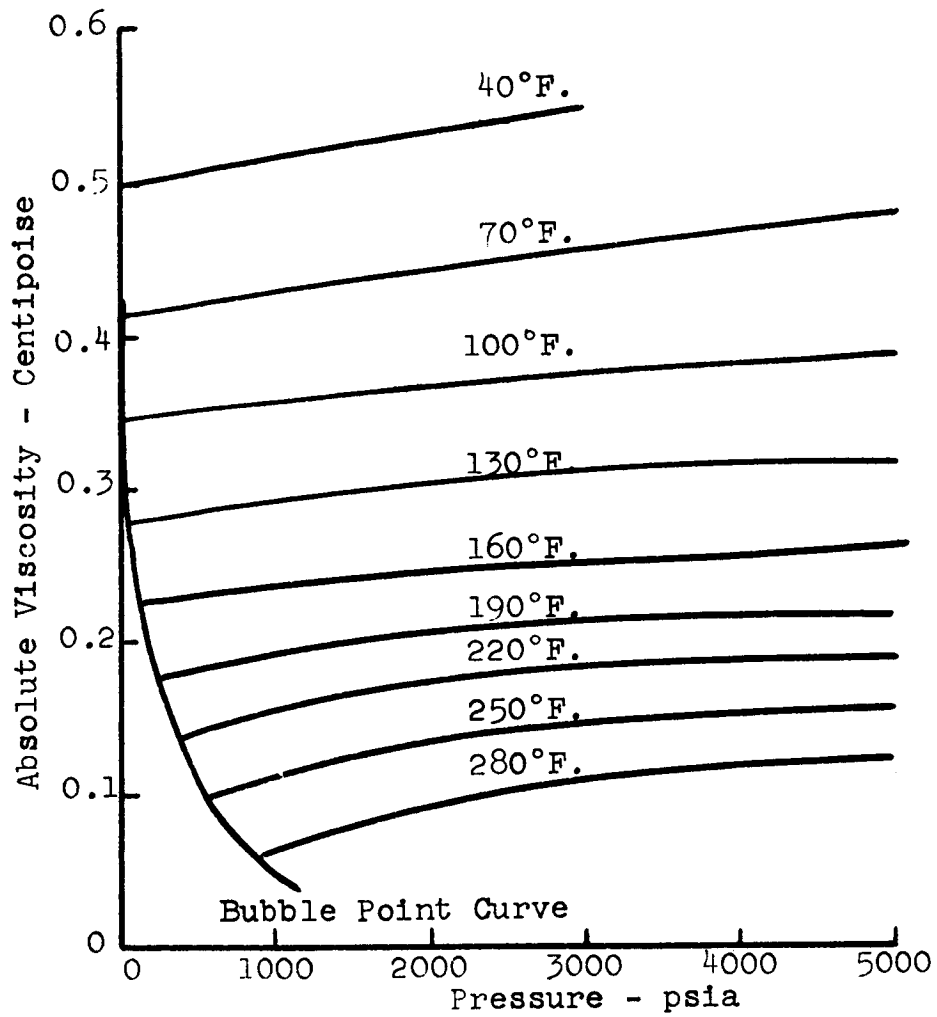


Figure 4-13

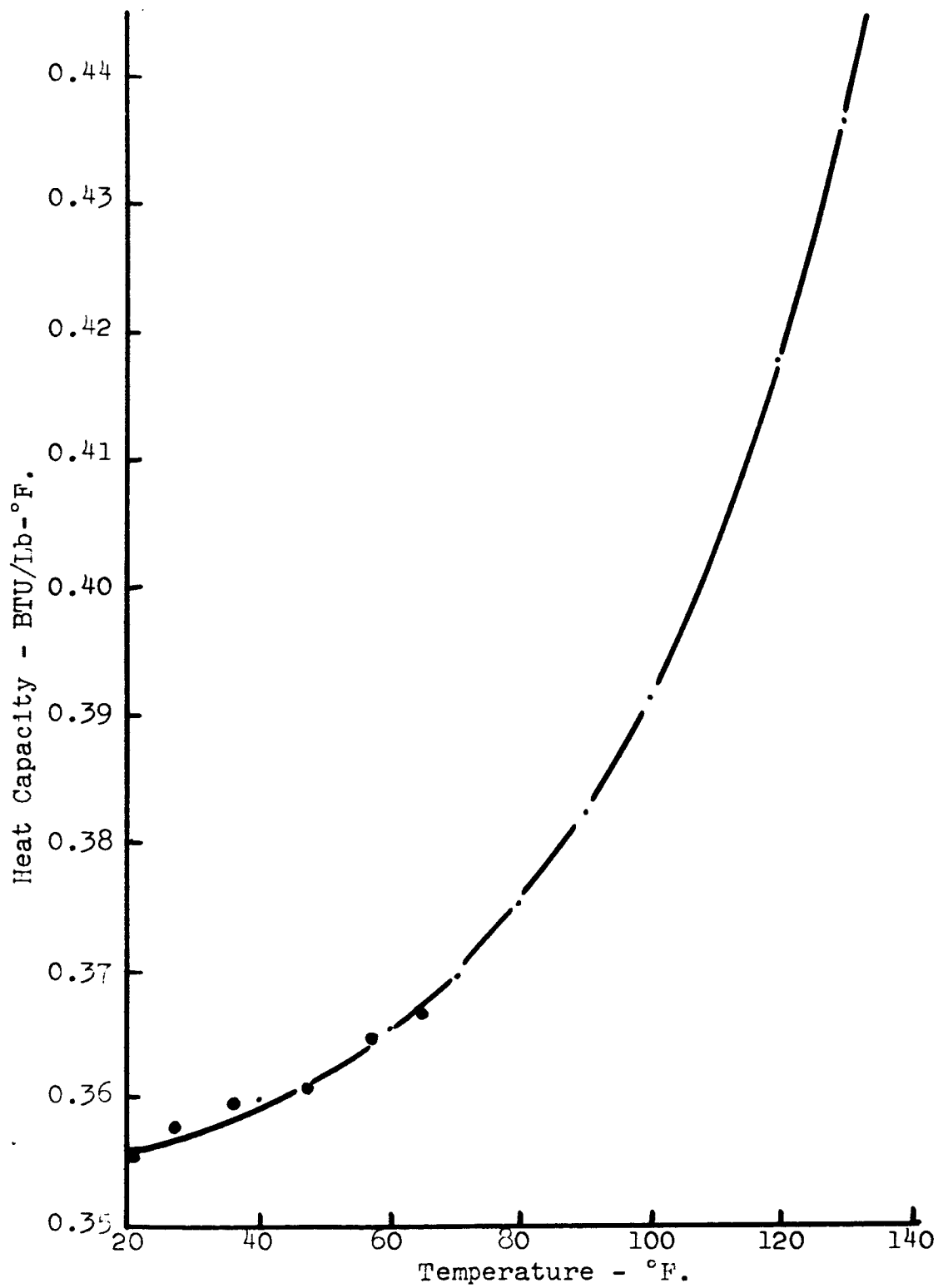
EFFECTS OF PRESSURE ON VISCOSITY,  
LIQUID  $N_2O_4$



(Reference 1)

Figure 4-14

HEAT CAPACITY OF LIQUID  $\text{N}_2\text{O}_4$



(Reference 7)

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K. Appendix

FINAL REPORT

Search of Technical Literature

TO: G. C. Mattson

FROM: Lewis F. Hatch

The following abstract journals were searched for the ten-year period 1955-1964: Chemical Abstracts, Zentralblatt. All of the pertinent abstracts found in the German abstract journal were also in Chemical Abstracts. The topics covered were hydrazine, unsymmetrical dimethyl-hydrazine and nitrogen tetroxide. The subheadings were physical properties and spectra, chemical properties, decomposition and decomposition products and analysis for the parent compounds and their decomposition products. Additional keywords were air pollution, atmospheric pollution, rockets, fuels and propellants.

The following government publications were not searched because they were not available and because they are abstracted by Chemical Abstracts: Governmentwide Index, International Aerospace Abstracts, Scientific and Technical Aerospace Reports, Technical Abstract Bulletin, U. S. Government Research Reports. The Rice University Library was searched for information which might have been absent from The University of Texas Library. None was found.

Xerox copies were made of about thirty (30) of the most interesting abstracts and of about ten (10) of the most interesting articles. These copies were sent to Jerry LaCoume to make the information available within the shortest possible time. We have brief abstracts of all the abstracts which are listed in this report. They can be made available if desired.

The literature gave no evidence of reaction between either hydrazine, UDMH, or nitrogen tetroxide and fluoro-compounds of the Freon<sup>®</sup> type.

References

\*Xerox copy of abstract sent to LaCoume

#Xerox copy of article sent to LaCoume

GENERAL

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### Analysis

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Figure 2-13

REMOVAL OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER  
USING ISOBUTANOL VAPORS AT 100°C.

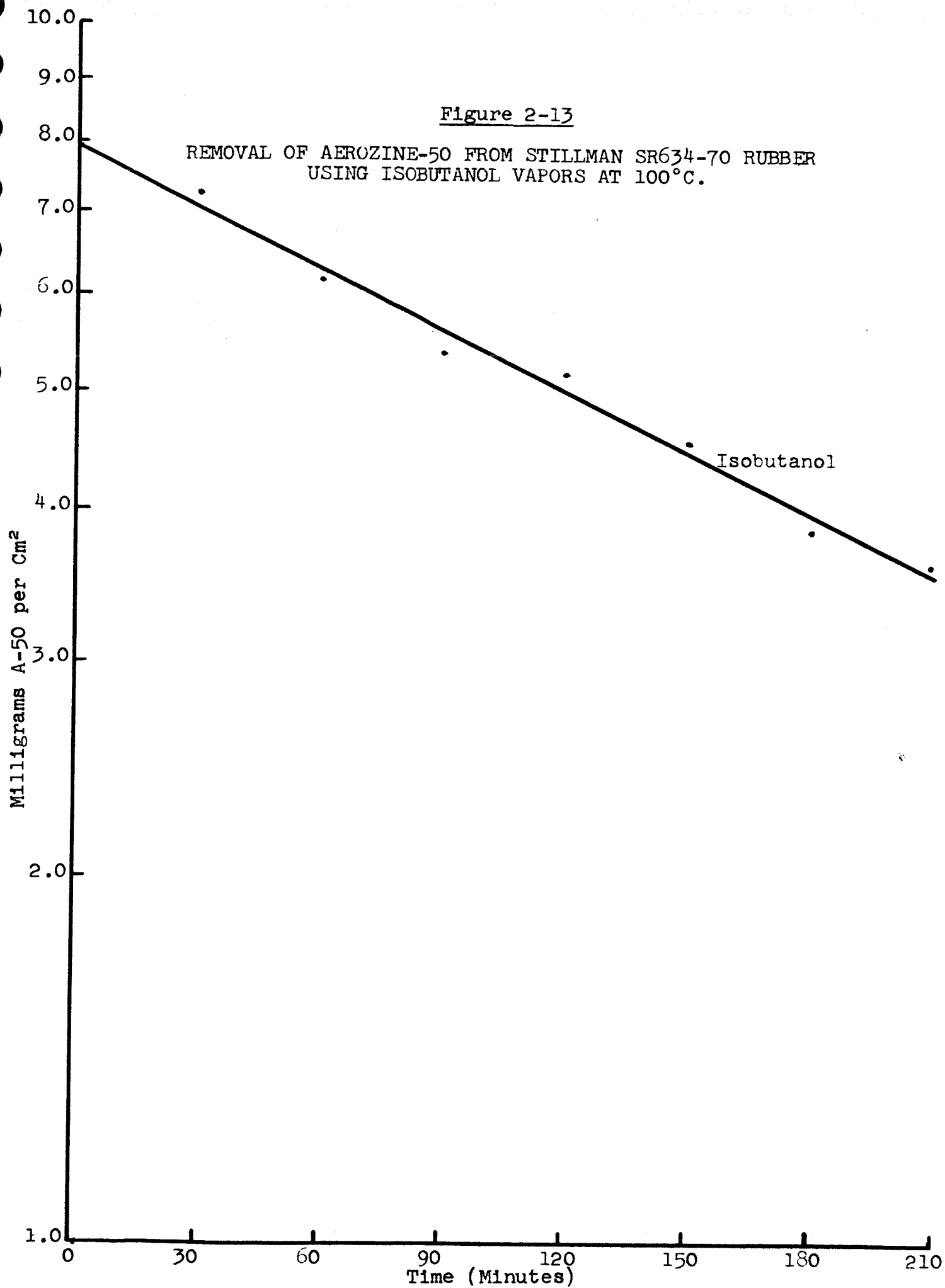
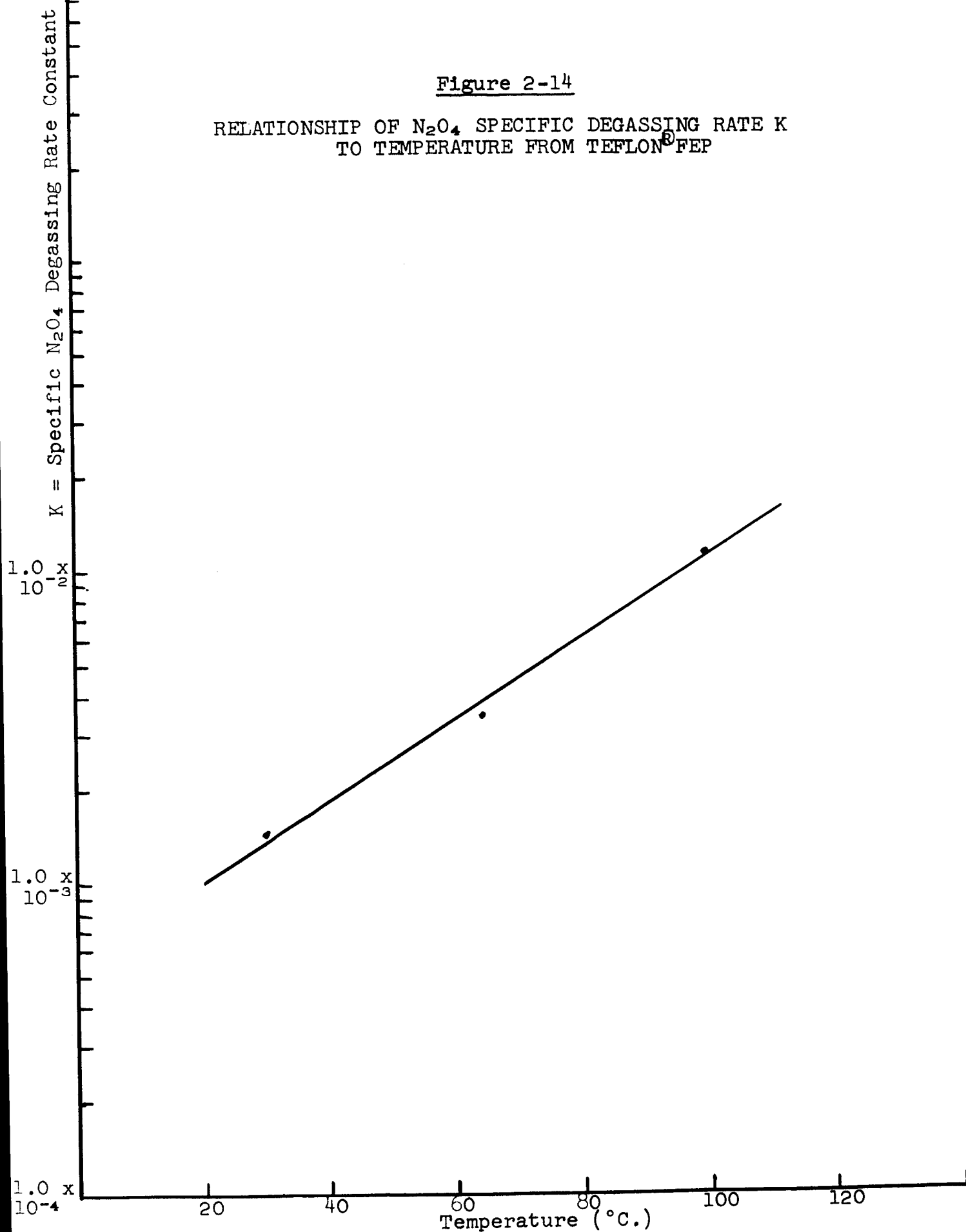


Figure 2-14

RELATIONSHIP OF  $\text{N}_2\text{O}_4$  SPECIFIC DEGASSING RATE K  
TO TEMPERATURE FROM TEFLON<sup>®</sup> FEP



## IX. UNIT 3 - METHODS RESEARCH

### A. Summary

1. Results obtained clearly show that the rate of desorption of  $N_2O_4$  from the Teflon<sup>®</sup> and of Aerozine-50 from Stillman SR634-70 rubber is dependent on temperature and independent of the kind of the solvent used.
2. Cleaning of the fuel and oxidizer systems may be accomplished by heating to temperatures in the range, 80 to 105° C, for a period of 1 to 3 hours, plus some form of purging. At ambient temperature, 1 to 5 days would be required.
3. Vapor-phase cleaning is feasible with a number of solvents, preferably those boiling in the range, 45° to 105° C.
4. Vapor-phase cleaning has advantages over liquid fill-and-drain procedures as follows:
  - a. Latent heat of vaporization of solvent available to heat the system uniformly throughout.
  - b. Flowing film of condensed solvent vapor is effective in removing solid as well as liquid contaminants.
  - c. All surfaces within the system are bathed by the flowing condensate film.
  - d. Solvent required is reduced by a factor varying from 1/100 to 1/1000 of the amount required for fill-and-drain flushing.
5. From a purely technical standpoint, the best vapor-phase decontaminating solvent is Freon<sup>®</sup> E-2, a development stage compound material produced by E. I. du Pont. It is compatible with all components of both systems.
6. Other solvents that may be suitable for use in vapor-phase decontamination are:
  - a. Inhibited carbon tetrachloride - oxidizer system
  - b. Isopropanol - fuel system
  - c. Methanol - fuel system

The objectives of this work unit include a search for unique and improved methods of decontaminating the propulsion system; a comparison of liquid-phase flushing with a vapor-phase process, and a study of the effect of temperature on the rate of removal of the oxidizer, the fuel, and selected solvents.

## B. Experimental and Results

Specimens cut from Teflon<sup>®</sup> TFE and Teflon<sup>®</sup> FEP were weighed and placed in test chambers. Liquid N<sub>2</sub>O<sub>4</sub> was added to the test chambers. The samples were submerged in the N<sub>2</sub>O<sub>4</sub> for a period ranging between 16 and 20 hours. The N<sub>2</sub>O<sub>4</sub> was drained off, the chambers purged with gaseous nitrogen (GN<sub>2</sub>) for 10 minutes, the specimens were removed, the weight gain was determined, and the specimens were returned to the test chambers. The specimens were decontaminated by the following procedures:

The first of these procedures was flushing with the solvent under test at ambient temperature. Each specimen was flushed a given number of times and allowed to drain. The specimen was removed from the chamber and the weight loss determined.

At 24.5° C the effectiveness of water, CCl<sub>4</sub>, and Freon<sup>®</sup> 11 as liquids, Freon<sup>®</sup> 11 as vapor, and gaseous nitrogen in removing N<sub>2</sub>O<sub>4</sub> from Teflons<sup>®</sup> was determined and compared with the rate N<sub>2</sub>O<sub>4</sub> degasses from a contaminated specimen in a desiccator.

These data are plotted in Figure 3-3. The curves in the figure show the rate of removal of N<sub>2</sub>O<sub>4</sub> from the specimens is roughly the same for all of the solvents under test. It requires about 400 minutes to remove one-half of the N<sub>2</sub>O<sub>4</sub> from the system. The rate of desorption decreases as the concentration of N<sub>2</sub>O<sub>4</sub> decreases so the remaining N<sub>2</sub>O<sub>4</sub> desorbs more slowly.

As the N<sub>2</sub>O<sub>4</sub> was desorbing from the test specimens, absorption of the cleansing solvent caused discrepancies in the data. Tests were made to determine the rate of absorption of CCl<sub>4</sub> by Teflon<sup>®</sup> TFE specimens submerged in the liquid at 24.5° C. The results are plotted in Figure 3-1.

The rate of solvent absorption by Teflon<sup>®</sup> TFE specimen suspended in the saturated vapor of the boiling solvents was determined for CCl<sub>4</sub> (b.p. = 81° C) and Freon<sup>®</sup> 112 (b.p. = 93° C). The results are shown by the curves in Figure 3-2. The effect of temperature is shown by comparing the absorption of CCl<sub>4</sub> for 400 minutes at 24.5° C and 81° C. The results show at 24.5° C approximately 0.06 mg/cm<sup>2</sup> of CCl<sub>4</sub> were absorbed compared to 0.70 mg/cm<sup>2</sup> at 81° C.

The effect of elevated temperature on the rate of desorption of the contaminants, N<sub>2</sub>O<sub>4</sub> and A-50, was investigated. Teflon<sup>®</sup> specimens contaminated with N<sub>2</sub>O<sub>4</sub> or Stillman SR634-70 rubber specimens contaminated with A-50 were suspended in the saturated vapor of the candidate solvent. The rate the respective contaminated specimen lost weight and the uncontaminated specimen gained weight was determined at timed intervals.

To correct for solvent absorption, the above contaminated specimens were each paired with uncontaminated or "blank" specimens. Five such pairs were usually placed in the saturated vapor of the candidate solvent. This work was done in ordinary refluxing apparatus. At timed intervals pairs were withdrawn from the vapor and weighed. The weight gain of the blank specimen of a given pair was assumed to indicate the amount of solvent the contaminated specimen had absorbed so this weight was deducted from the gross weight of the contaminated specimen to give a measure of the net contaminant remaining in the specimen. The assumption that equal amounts of solvent would be absorbed in both members of the specimen pairs proved to be in error in some instances. The curves in Figures 3-4, 3-5, and 3-6 show the contaminated Stillman rubber specimens absorbed more of some solvents than the uncontaminated or blank specimens.

Figure 3-3 shows the effect of increasing the temperature of  $\text{CCl}_4$  from  $24.5^\circ \text{C}$  to  $81^\circ \text{C}$  on the rate of desorption. Weight change data corrected as described above is plotted against time. At  $24.5^\circ \text{C}$  in 200 minutes, a Teflon<sup>®</sup> TFE specimen had lost 36.2% of its  $\text{N}_2\text{O}_4$  content. In the same time interval at  $81^\circ \text{C}$ , an identical specimen had lost 91.7% of its  $\text{N}_2\text{O}_4$  content. This figure also shows the desorption of  $\text{N}_2\text{O}_4$  from Teflon<sup>®</sup> TFE at  $93^\circ \text{C}$ --the boiling point of Freon<sup>®</sup> 112. Extrapolation of this curve indicates that the  $\text{N}_2\text{O}_4$  content in the Teflon<sup>®</sup> would drop to zero in roughly 200 minutes.

The absorbed solvent is considered to be a contaminant as well as the oxidant or the fuel, though less objectionable in some instances. Therefore, attention was given to the possibility that heated nitrogen might drive out the solvent remaining in the nonmetallic parts after the solvent had driven out the contaminant.

The results of desorption of A-50 from Stillman SR634-70 are shown by the curves in Figure 3-5. Inspection of the curves shows that desorption of the A-50 is obscured by the absorption of water. One pair of specimens was placed in a  $50^\circ \text{C}$  nitrogen stream without any steam treatment. Desorption of the A-50 from the contaminated specimen based on weight change of this pair at  $50^\circ \text{C}$  was plotted against time. It is shown by the lower of the curves originating at the 8.0 milligram per square centimeter ordinate value. Five other pairs of specimens were placed in the saturated steam in the refluxing column and were withdrawn at timed intervals. The specimens were weighed, then placed in the  $50^\circ \text{C}$  nitrogen stream. The weight loss in the  $50^\circ \text{C}$  nitrogen stream is shown as the curves branching from the "A-50 reflux desorption" curve. Similar data was plotted for methanol (Figure 3-6), isopropanol (Figure 3-7), and Freon<sup>®</sup> E-2 (Figures 3-9, 3-10, and 3-11).

The curves show the desorption of absorbed materials from the Stillman rubber in the  $50^\circ \text{C}$  nitrogen stream is very slow whether it be water, or A-50, or a mixture.

The initial concentration of A-50 in Stillman rubber affects the desorption rate. The curves in Figure 3-5 are plots of weight change of Stillman rubber in which the initial concentration of A-50 was 5.0 mg/cm<sup>2</sup> in one specimen and 8.0 mg/cm<sup>2</sup> in the other. The rapid weight loss of the specimen starting with 5.0 mg/cm<sup>2</sup> was rapid whereas the specimen with 8.0 mg/cm<sup>2</sup> showed an increase in weight.

The curves in Figure 3-7 show the results of work with isopropanol in removing A-50 from Stillman rubber. Inspection of the curves shows the A-50 is rapidly expelled if the weight change correction is applied. The Stillman rubber absorbed more isopropanol than was experienced with methanol, steam, and several other solvents.

Figure 3-8 is a plot of data obtained with perfluorodimethylcyclobutane. The rate of desorption of A-50 from Stillman rubber based on weight change measurements is slow, because of the low boiling temperature of this solvent, 45° C. One-half of the A-50 had been desorbed in about 1,300 minutes, which is about the same desorption rate of A-50 in 50° C, GN<sub>2</sub>.

One of the more important aspects of this work is the discovery that absorption of perfluorodimethylcyclobutane into the Stillman rubber is very slight--less than 0.1 milligram per square centimeter in 24 hours at 45° C. This solvent was disqualified for use in fuel system decontamination because of the formation of a solid reaction product which appeared as a scum on the wall of the flask.

Figure 3-9 shows a plot of data obtained with a second fluorinated compound, du Pont's Freon® E-2 (b.p. = 101° C), a fluorinated ether. Contaminated test specimen suspended in the saturated vapor of boiling Freon® E-2 desorbed the A-50 in 5 to 6 hours with negligible absorption of this solvent in the specimens. This solvent appears to be ideal for use in decontamination of the fuel system. It is extremely inert and has no detrimental effects on the physical properties of Stillman rubber.

Figures 3-10 and 3-11 show plots of data obtained in tests on specimens of Teflon® TFE and FEP, respectively, desorbing N<sub>2</sub>O<sub>4</sub> in the saturated vapor of Freon® E-2. The desorption proceeds rapidly. TFE is completely free of N<sub>2</sub>O<sub>4</sub> in 50 minutes. FEP requires 5 to 7 hours. Adsorption of the Freon® E-2 into the Teflons® was appreciable.

Tables 3-I and 3-II summarize results plotted in Figures 3-1 through 3-11 and give additional information relative to the solvents tested.

### C. Discussion

The general approach was based on the premise that most of the difficulties in the decontamination procedures are due to propellants absorbed into semiporous elastomers and plastic materials in the systems. Work in the unit was entirely concerned with studies to determine the most effective way to decontaminate these non-metallic materials with the least possible detrimental effect on them or on the metallic parts.



Also, total decontamination of the nonmetallic parts was considered to be a proper goal even though not completely attainable. That is, not only were the respective propellant components to be removed but also the cleansing solvent so that the part would be free of any foreign substance.

It was at first expected that liquid-or vapor-flushing at ambient temperature would probably suffice for decontamination. The problem was thought to be merely that of determining which solvent was the most effective in leaching out the respective propellant components.

It is considered difficult to heat the propulsion system to the desired temperature range by flowing heated gas through the system. The sensible heat available by this means would not be sufficient to maintain the desired temperature because of radiation, conduction, and convection losses.

By vaporizing a fluid and flowing the vapor through the system, the latent heat of vaporization is available to allow uniform heating throughout the system. The vapor would condense on all surfaces colder than the boiling point of the solvent. These surfaces would be bathed in a flowing film of the condensing vapor while at the same time being heated. Heating by this means would be rapid and uniform. The uncondensed vapor flowing through the systems would sweep out the gas phase of the contaminants. The amount of solvent required for vapor-phase flushing is less by a factor of between 1/100 and 1/1000 than would be required for a liquid flush procedure. Vapor-phase flushing should be feasible for the decontamination of both the fuel and the oxidizer systems.

The most effective decontaminating solvent for use in vapor-phase flushing is Freon<sup>®</sup> E-2. However, this solvent is in the developmental stage. Vapor-phase flushing would require about 1,000 pounds for the Apollo propulsion system.

Freon<sup>®</sup> E-2 would be suitable for decontaminating both systems. It is interesting to note that Freon<sup>®</sup> E-2 has a molecular weight of 452; it has only one hydrogen atom and two oxygen atoms; otherwise, it is a totally fluorinated ether. There are not many compounds that meet all requirements, but other compounds that might be expected to have merits similar to Freon<sup>®</sup> E-2 as a decontaminant would have these properties:

1. Inertness to  $N_2O_4$  and A-50.
2. Molecular weight in the range of 300 and up for low absorption.
3. Low freezing point,  $-10^{\circ}C$  or lower.
4. Boiling point in the range,  $80-101^{\circ}C$ . This, with a large molecular weight, would also require a highly fluorinated compound.

Other solvents that may be suitable for decontamination are inhibited  $CCl_4$ , in the oxidizer system, and isopropanol, normal propanol, or methanol, in the fuel system. The Stillman rubber absorbs significant

amounts of these materials and holds them tenaciously. However, it is believed that the presence of these compounds can be tolerated to the extent that they would be present in the fuel system.

Water would be excellent and cheap for use in both systems, but there are widespread objections to water because of the difficulties of complete drying.

TABLE 3-1 REMOVAL OF  $N_2O_4$  FROM TEFLONS<sup>(B)</sup> TFE AND FEP

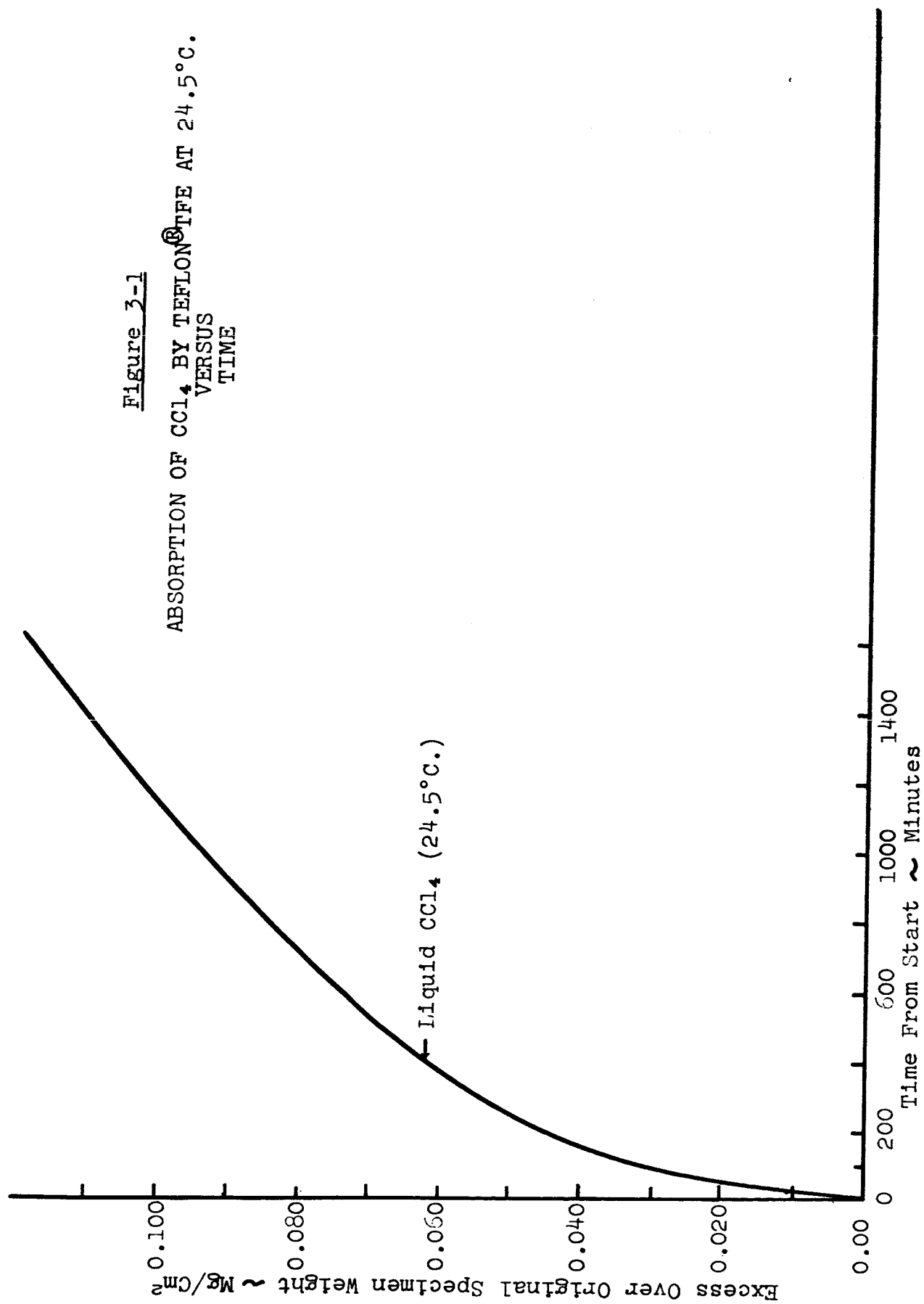
TABLE 3-1 REMOVAL OF  $N_2O_4$  FROM TEFLONS<sup>(B)</sup> TFE AND FEP

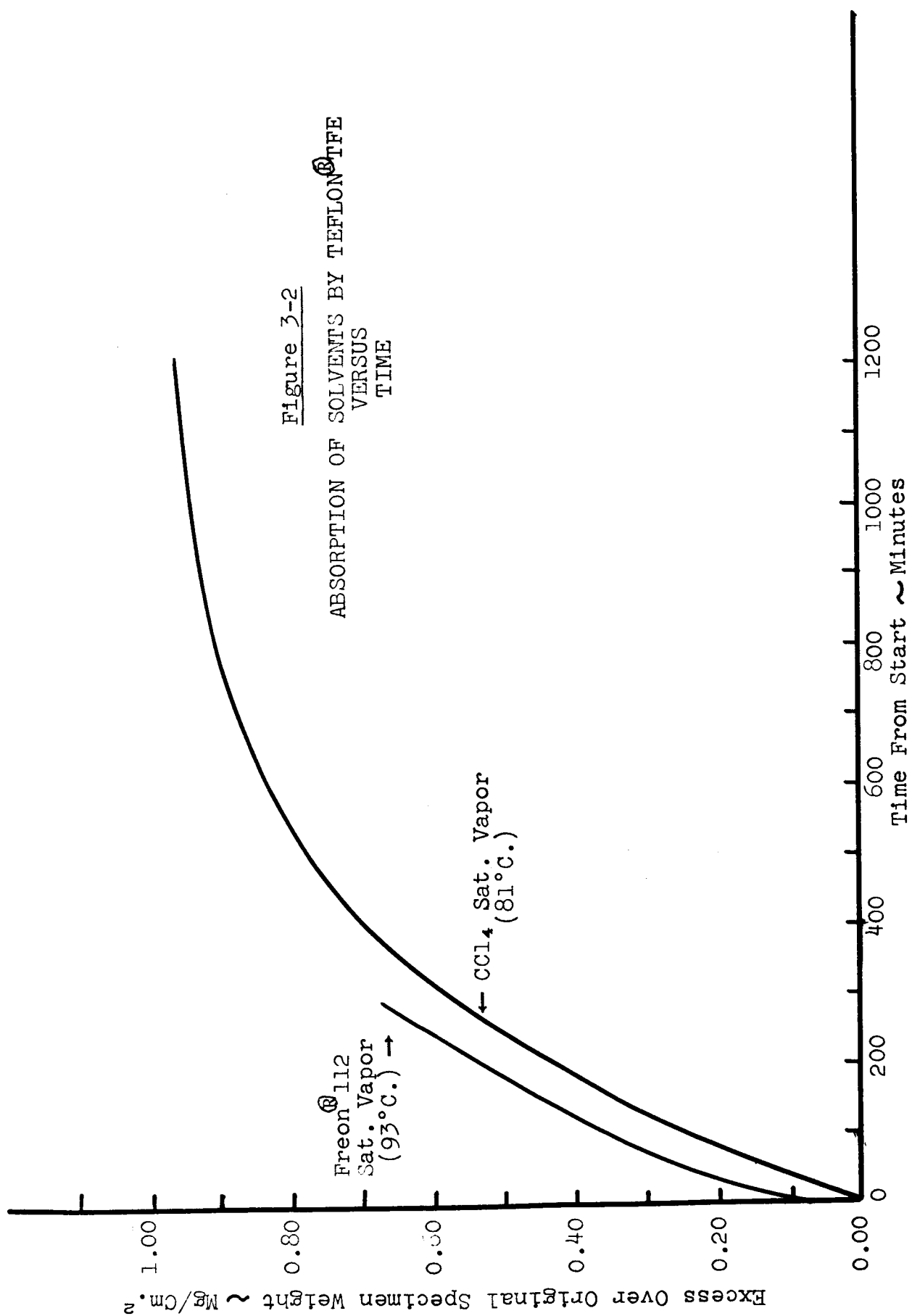
Cleaning Solvent, Vapor, or Gas Tested and Type of Teflon Used	Plot Fig. No.	Formula	Boiling Point or Temp of Test °C	Effect of Solvent on Tensile Strength (See Note 1)	Net Weight Change of N <sub>2</sub> O <sub>4</sub> Treated Specimens and Weight Gain of Blank Specimens Due to Solvent Absorption as Percent of Initial Weight of N <sub>2</sub> O <sub>4</sub> Absorbed in Treated Specimens at Indicated Time Intervals								Remarks
					50 Minutes		100 Minutes		300 Minutes		1,400 Minutes		
					Treated	Blank	Treated	Blank	Treated	Blank	Treated	Blank	
Carbon Tetrachloride Teflon 8 TFE	1, 3	CCl <sub>4</sub>	24.5	Negligible	(Loss) 17.8	(Gain) 0.61	(Loss) 24.1	(Gain) 2.0	(Loss) 44.4	2.9	--	6.2	
Water (TFE)	3	H <sub>2</sub> O	24.5	Negligible	(Loss) 19.5	--	(Loss) 29.0	--	--	--	--	--	
Freon 11 Liquid (TFE)	3	CCl <sub>3</sub> F	24.5	Negligible	(Loss) 18.3	--	(Loss) 26.7	--	--	--	--	--	
Freon 11 Vapor (TFE)	3	CCl <sub>3</sub> F	24.5	Negligible	(Loss) 13.9	--	(Loss) 20.5	--	--	--	--	--	
Nitrogen Purge (TFE)	3	GN <sub>2</sub>	24.5	None	(Loss) 22.0	--	(Loss) 32.7	--	--	--	--	--	
Desiccator (TFE)		Dry Air	24.5	None	(Loss) 27.3	--	(Loss) 34.5	--	--	--	--	--	100% Desorp- tion at 260 minutes
Carbon Tetrachloride (TFE)	2, 3	CCl <sub>4</sub>	81°	Negligible	(Loss) 61.1	(Gain) 6.7	(Loss) 76.1	(Gain) 12.8	(Loss) 100.0	(Gain) 32.0	--	--	Extrapolated Curve would be at 100% Desorption at 200 minutes
Freon 112 (TFE)	3	C <sub>2</sub> Cl <sub>4</sub> F <sub>2</sub>	93°	Negligible	(Loss) 66.1	(Gain) 12.8	(Loss) 78.9	(Gain) 19.4	(Loss) 100.0	(Gain) 37.2	--	--	
Freon E-2 (TFE)	11	$\begin{matrix} \text{F} & \text{F} \\   &   \\ \text{F}[\text{C}-\text{C}-\text{O}]_2 \\   &   \\ \text{CF}_3 & \text{F}-\text{C}-\text{F} \\ &   \\ & \text{F}-\text{C}-\text{F} \\ &   \\ & \text{F} \end{matrix}$	101°	Negligible	(Loss) 100	(Gain) 25.0	--	--	--	--	--	--	
Freon E-2 (FEP)	12	$\begin{matrix} \text{F} & \text{F} \\   &   \\ \text{CF}_3 & \text{F}-\text{C}-\text{F} \\ &   \\ & \text{F}-\text{C}-\text{F} \\ &   \\ & \text{F} \end{matrix}$	101°	Negligible	(Loss) 60.0	(Gain) 6.0	(Loss) 78.0	(Gain) 16.0	(Loss) 96.0	(Gain) 36.0	(Loss) 100.0	100% Desorp- tion at 500 minutes	

TABLE 3-II REMOVAL OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER

Cleaning Solvent, Vapor or Gas Tested	Plot Fig. No.	Formula	Boiling Point or Temp of Test	Aerozine-50 Absorbed by Specimens mg/cm <sup>2</sup> (Avg.)	Net Weight Change of Refluxing Specimens Treated with A-50 and Weight Gain of Blank Specimens as Percent of Initial Weight of A-50 Absorbed in Treated Specimens at Indicated Time Intervals										Remarks
					50 Minutes		100 Minutes		300 Minutes		1,400 Minutes				
					(Loss) Treated	(Gain) Blank	(Loss) Treated	(Gain) Blank	(Loss) Treated	(Gain) Blank	(Loss) Treated	(Gain) Blank			
Du Pont Freon <sup>®</sup> E-2	10	$\begin{array}{c} \text{F} \quad \text{CF} \quad \text{CF}_2 \quad \text{O}_2 \\   \quad   \quad   \\ \text{CF}_3 \quad \text{HCF} \quad \text{F} \\   \\ \text{F}-\text{C}-\text{F} \\   \\ \text{F} \end{array}$	101° C	7.5	(Loss) 65.3	(Gain) 0	(Loss) 78.6	(Gain) 0	(Loss) 92.0	(Gain) 0	(Loss) 100	(Gain) 6.7	Suitable for cleaning both fuel and oxidant systems		
Saturated Steam	6	H <sub>2</sub> O	100° C	8.0	(Gain) 5.0	(Gain) 3.7	(Gain) 4.4	(Gain) 5.6	(Gain) 2.5	(Gain) 9.4	--	--	Suitable for cleaning both fuel and oxidant systems		
Mixture: 50% Ethanol 50% Acetone	4	$\begin{array}{c} \text{C}_2\text{H}_5\text{OH} \\   \\ \text{CH}_3-\text{CO}-\text{CH}_3 \end{array}$	68° C	5.0	(Gain) 26.0	(Gain) 20.0	(Gain) 32.0	(Gain) 26.0	(Gain) 44	(Gain) 42.0	--	--	Not suitable		
Methanol	7	CH <sub>3</sub> OH	65° C	7.5	(Gain) 9.5	(Gain) 2.0	(Gain) 11.4	(Gain) 3.3	(Gain) 11.7	(Gain) 5.3	--	--	Suitable for cleaning fuel system only		
Isopropanol	8	$\begin{array}{c} \text{OH} \\   \\ \text{CH}_3-\text{C}-\text{CH}_3 \\   \\ \text{H} \end{array}$	83° C	8.0	(Loss) 35.0	(Gain) 15.0	(Loss) 47.5	(Gain) 20.4	(Loss) 66.2	(Gain) 32.0	--	--	Suitable for cleaning fuel system only		
Nitrogen	6	GN <sub>2</sub>	50° C	8.0	(Loss) 5.5	(Gain) 0.0	(Loss) 8.75	(Gain) 0.0	(Loss) 23.1	(Gain) 0	(Loss) 58.7	(Gain) 0	Suitable for cleaning both fuel and oxidant systems		
Perfluorodimethylcyclobutane	9	$\begin{array}{c} \text{CF}_3 \quad \text{CF}_3 \\   \quad   \\ \text{F}-\text{C}-\text{C}-\text{F} \\   \quad   \\ \text{F} \quad \text{F} \end{array}$	45° C	8.5	(Loss) 8.9	(Gain) 0	(Loss) 12.3	(Gain) 0	(Loss) 23.3	(Gain) 0	(Loss) 42.1	(Gain) 1.76	Might be suitable for cleaning oxidant system forms solid reaction product with A-50 contaminated Stillman rubber. Disqualified for fuel SIOE cleaning.		

E. Figures





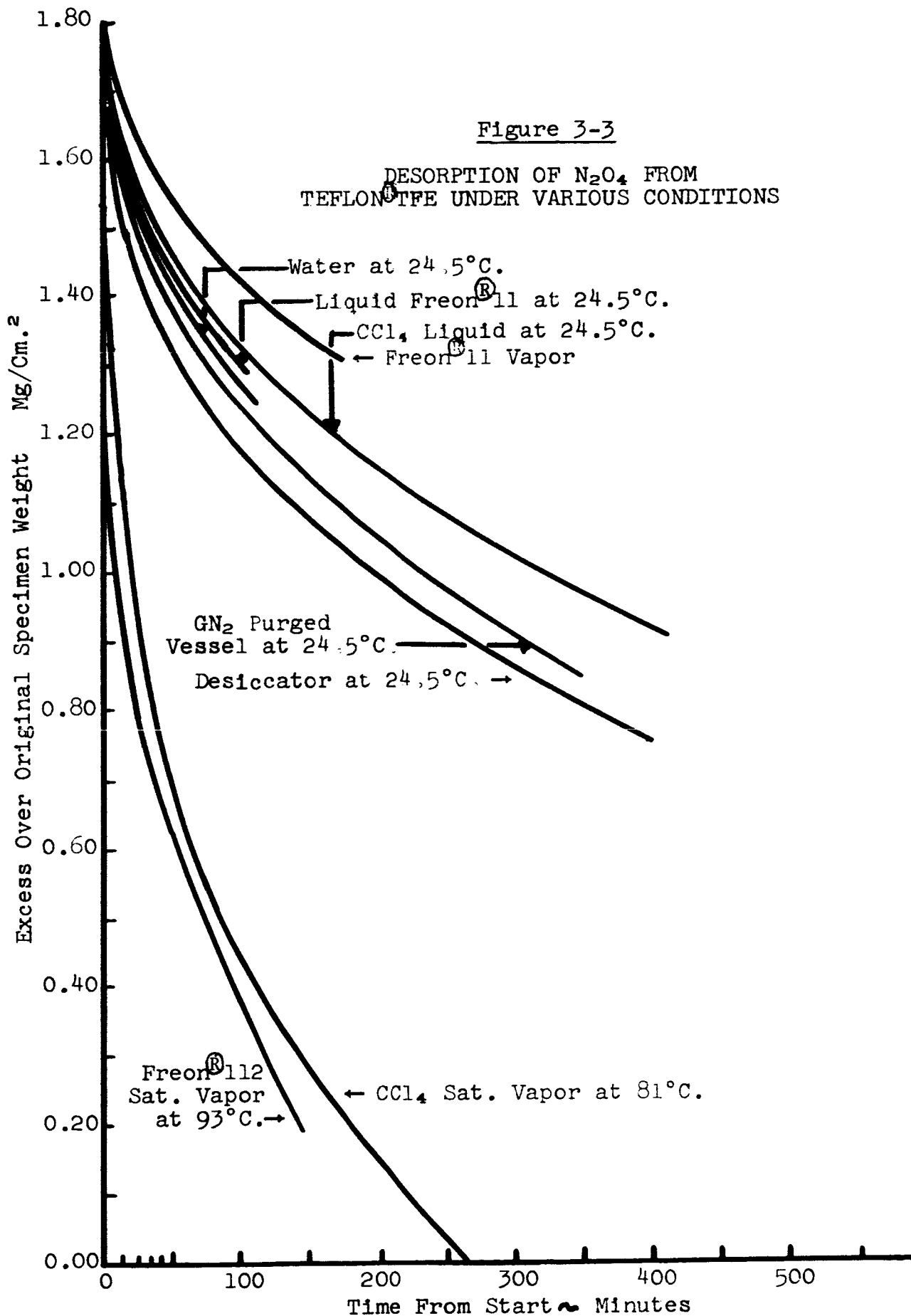


Figure 3-4

REMOVAL OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER  
WEIGHT CHANGES OF PAIRED SPECIMENS

REFLUXING IN:

50% ETHANOL (APPROX.) }  
50% ACETONE (APPROX.) } B.P.=68°C.

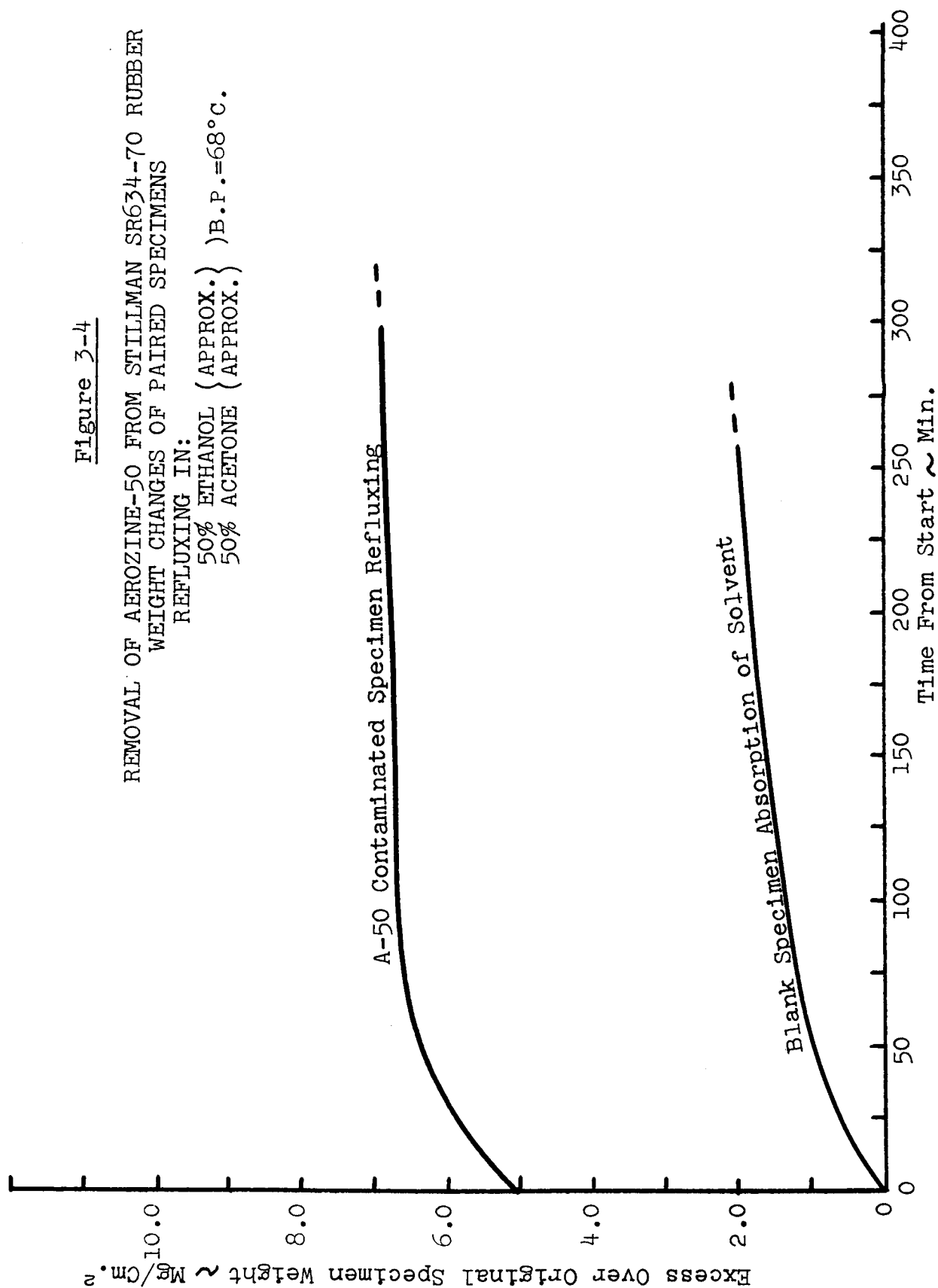




Figure 3-5

REMOVAL OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER  
WEIGHT CHANGES OF PAIRED SPECIMENS

1. REFLUXING IN SAT. STEAM AT 100°C.
2. DESORBING IN 50°C.  $\text{GN}_2$

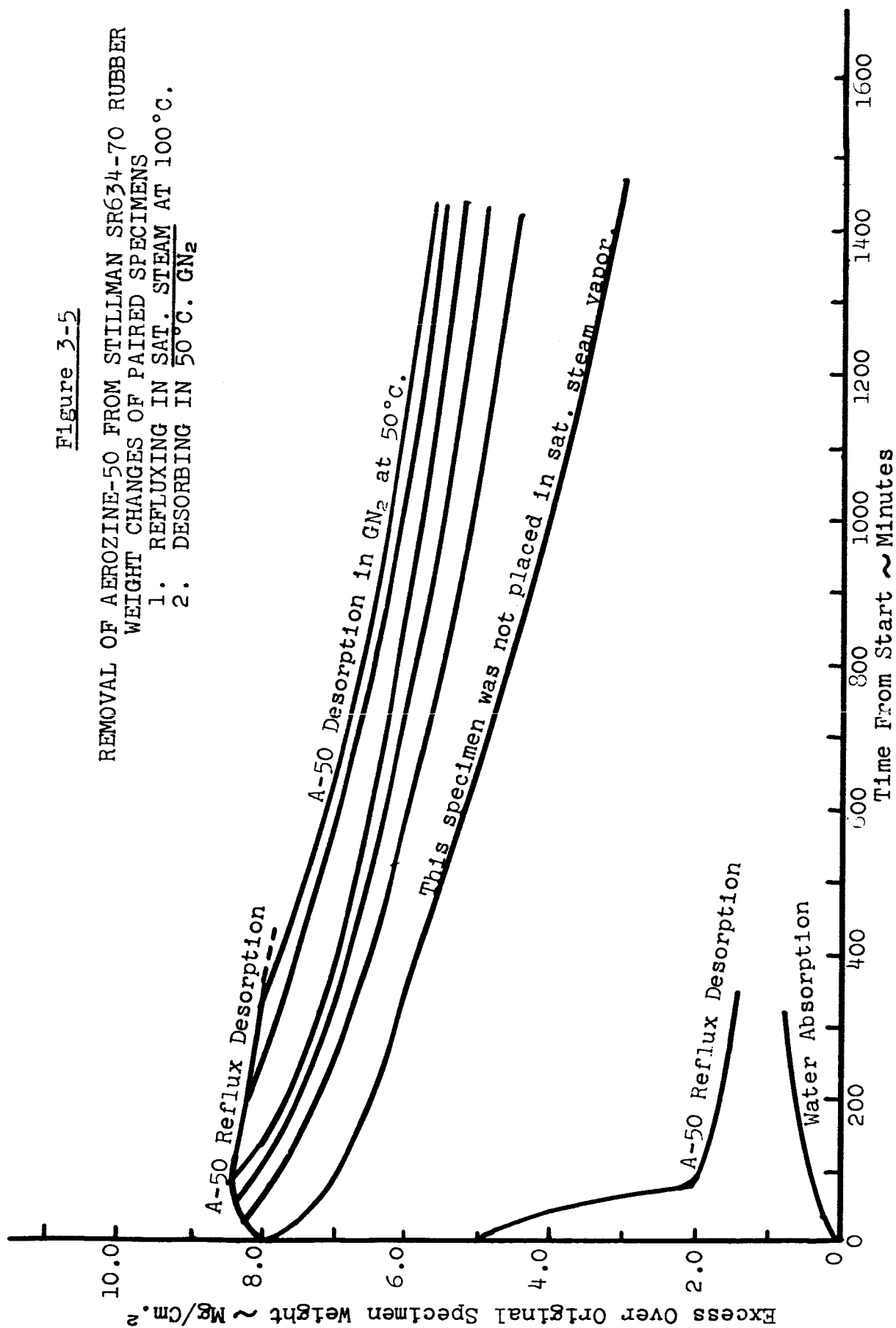


Figure 3-6

REMOVAL OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER  
WEIGHT CHANGES OF PAIRED SPECIMENS  
1. REFLUXING IN METHANOL (B.P.=65°C.)  
2. DESORBING IN 50°C. GN<sub>2</sub>.

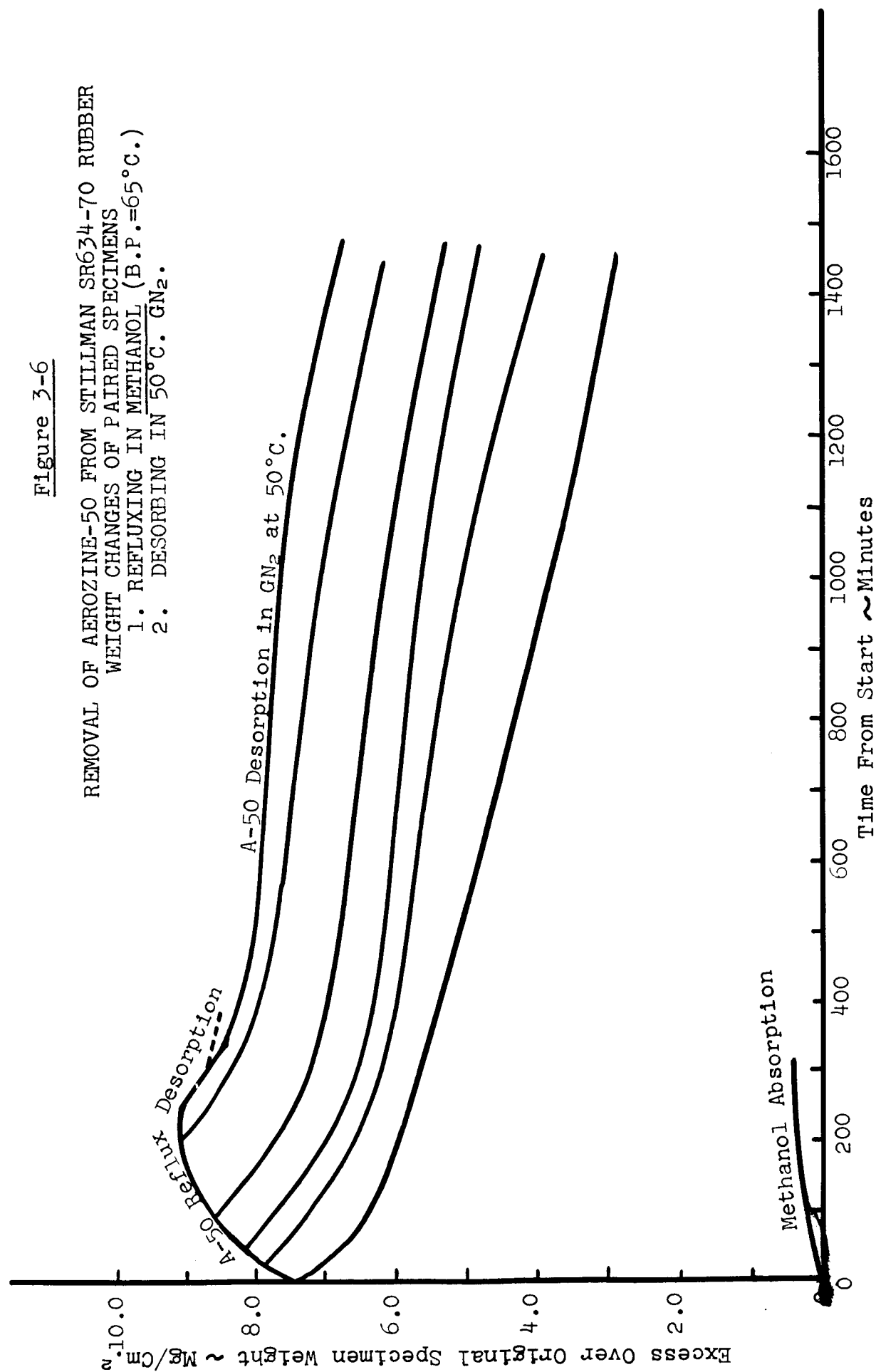


Figure 3-7

REMOVAL OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER

WEIGHT CHANGES OF PAIRED SPECIMENS

1. REFLUXING IN ISOPROPANOL (B.P.=83°C.)
2. DESORBING IN 50°C. GN<sub>2</sub>.

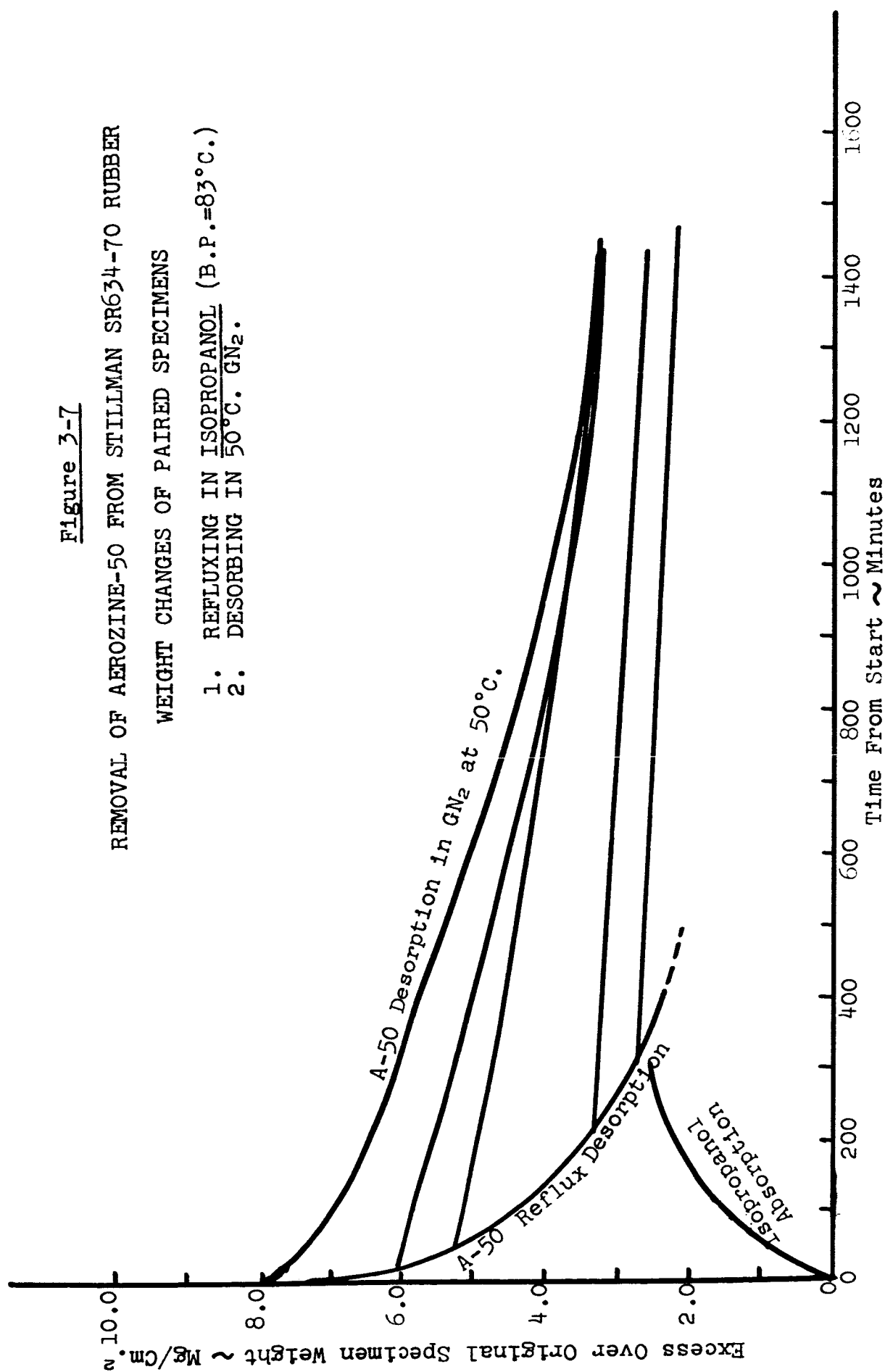


Figure 3-8

REMOVAL OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER

WEIGHT CHANGES OF PAIRED SPECIMENS

1. REFLUXING IN PERFLUORODIMETHYLCYCLOBUTANE  
AT 45°C.
2. DESORBING IN 50°C GN<sub>2</sub>.

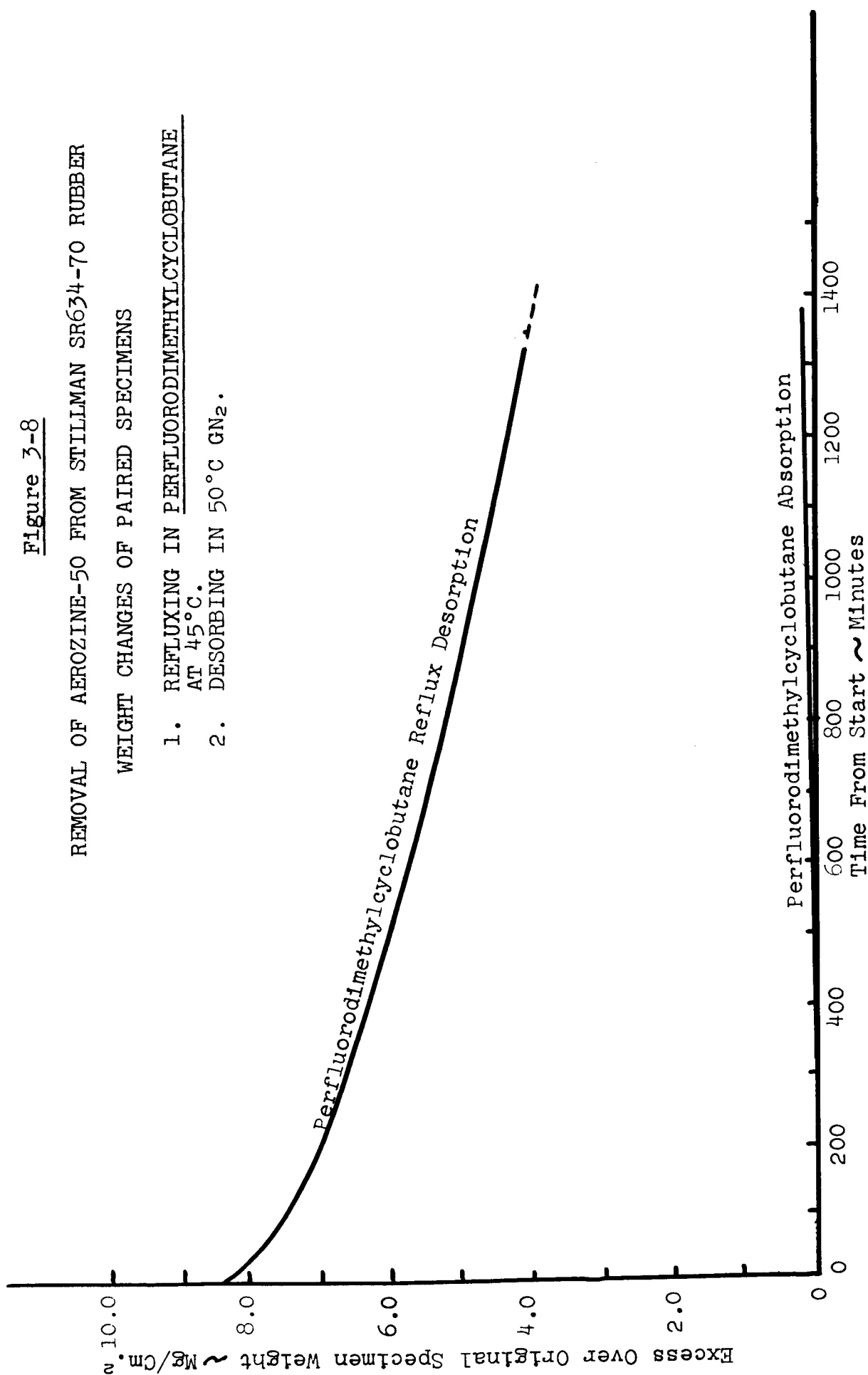


Figure 3-2

REMOVAL OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER

WEIGHT CHANGES OF PAIRED SPECIMENS

1. REFLUXING IN FREON<sup>®</sup> E-2 (B.P.=101°C.)
2. DESORBING IN 50°C. GN<sub>2</sub>.

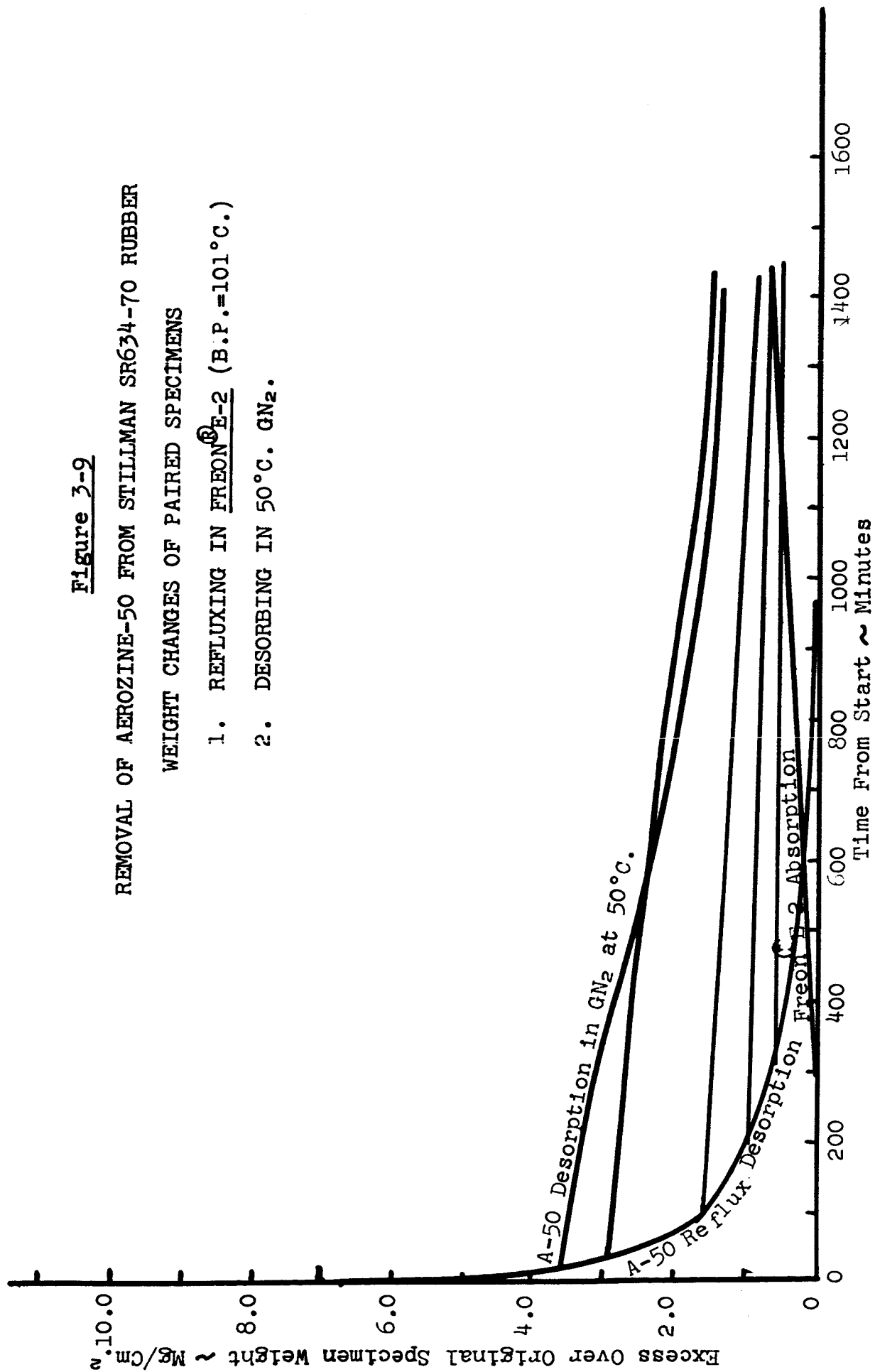


Figure 3-10

REMOVAL OF  $\text{N}_2\text{O}_4$  FROM TEFLON<sup>®</sup> TFE

WEIGHT CHANGES OF PAIRED SPECIMENS

1. REFLUXING IN FREON<sup>®</sup> E-2 (B.P.=101°C.)
2. DESORBING IN 50°C.  $\text{GN}_2$ .

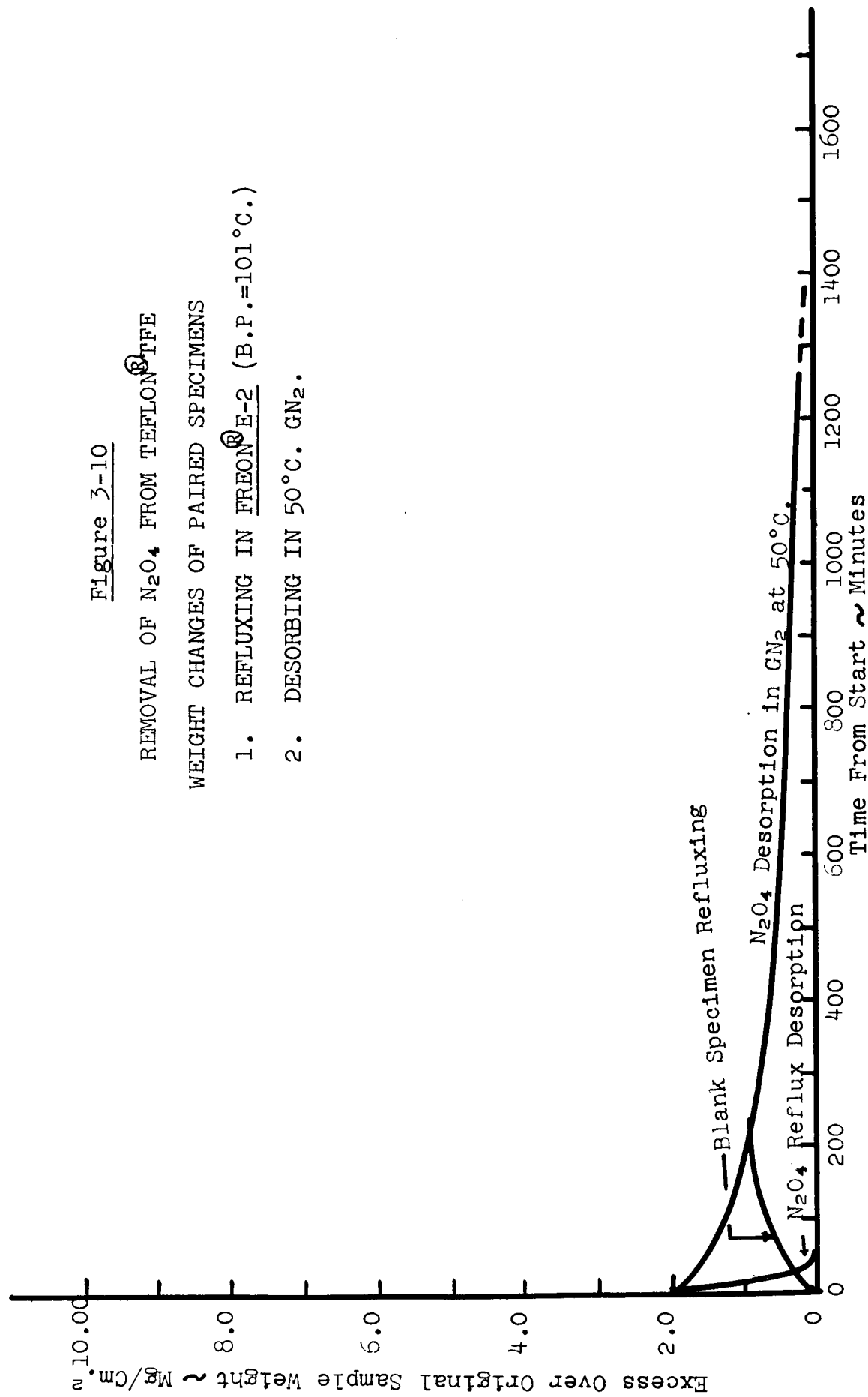
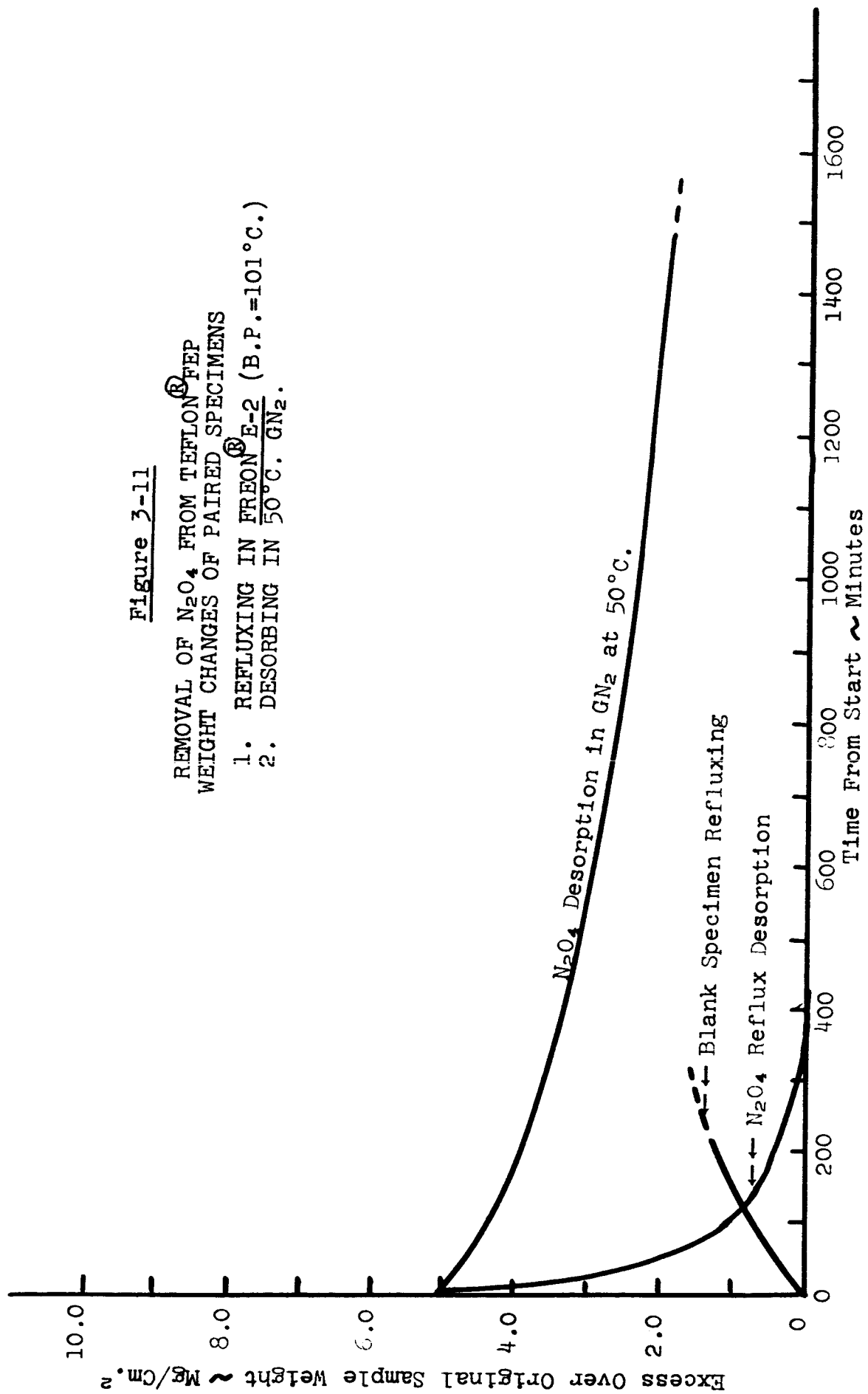


Figure 3-11

REMOVAL OF  $N_2O_4$  FROM TEFLON<sup>®</sup> FEP  
 WEIGHT CHANGES OF PAIRED SPECIMENS

1. REFLUXING IN FREON<sup>®</sup> E-2 (B.P.=101°C.)
2. DESORBING IN  $50^\circ\text{C. GN}_2$ .







## X. ANALYTICAL PROCEDURES

### A. Determination of Nitrogen Tetroxide in Aqueous Solution

#### 1. Scope

This method is applicable to the determination of nitrogen tetroxide in the range of 20 ppm or more in aqueous solution.

#### 2. Principle

In aqueous solution nitrogen tetroxide forms nitric and nitrous acids which are titratable with standard sodium hydroxide.

#### 3. Reagents

(a) Sodium hydroxide, standard 0.1 N, 0.01 N and 0.001 N solutions. Dilute 8 grams of clear 50% sodium hydroxide solution with distilled water and make to one liter volume. Standardize against 0.1 N hydrochloric acid which has been standardized against primary standard sodium carbonate. Prepare the 0.01 N and 0.001 N NaOH by diluting the 0.1 N solution with carbonate-free distilled water.

(b) Phenolphthalein indicator - 0.1% in ethanol.

#### 4. Interferences

Any acid or base present will represent an interference.

#### 5. Procedure

Pipet into a flask a volume of sample such that it contains a minimum of 250 micrograms of nitrogen tetroxide. Add two or three drops of phenolphthalein indicator and titrate to the first faint pink color that is stable for about 20 seconds. Use the most appropriate strength solution of sodium hydroxide. Calculate ppm nitrogen tetroxide.

#### 6. Calculation

$$\frac{\text{ml titrant} \times \text{normality titrant} \times 46,000}{\text{ml sample} \times \text{density sample}} = \text{ppm nitrogen tetroxide}$$

### B. Determination of Nitrogen Tetroxide in Organic Solvents

#### 1. Scope

This method may be used to determine nitrogen tetroxide in organic solvents down to the 20 ppm level.

## 2. Principle

Standard alcoholic potassium hydroxide is used to titrate  $\text{N}_2\text{O}_4$  or its acidic decomposition products. The end point of the titration is determined potentiometrically.

## 3. Interferences

As this is a simple acid-base titration, other acids or bases present will interfere.

## 4. Apparatus

pH meter, Leeds and Northrup 7401, or equivalent, equipped with glass and calomel electrodes.

## 5. Reagents

- (a) Ethanol, 95 to 100%.
- (b) Potassium hydroxide, standard 1 N, 0.01 N and 0.001 N solutions. Dissolve 16.7 grams of low-carbonate potassium hydroxide in ethanol and dilute to 250.0 ml. Standardize against primary standard benzoic acid. Prepare solutions of 0.01 N and 0.001 N potassium hydroxide by dilution with alcohol.

## 6. Procedure

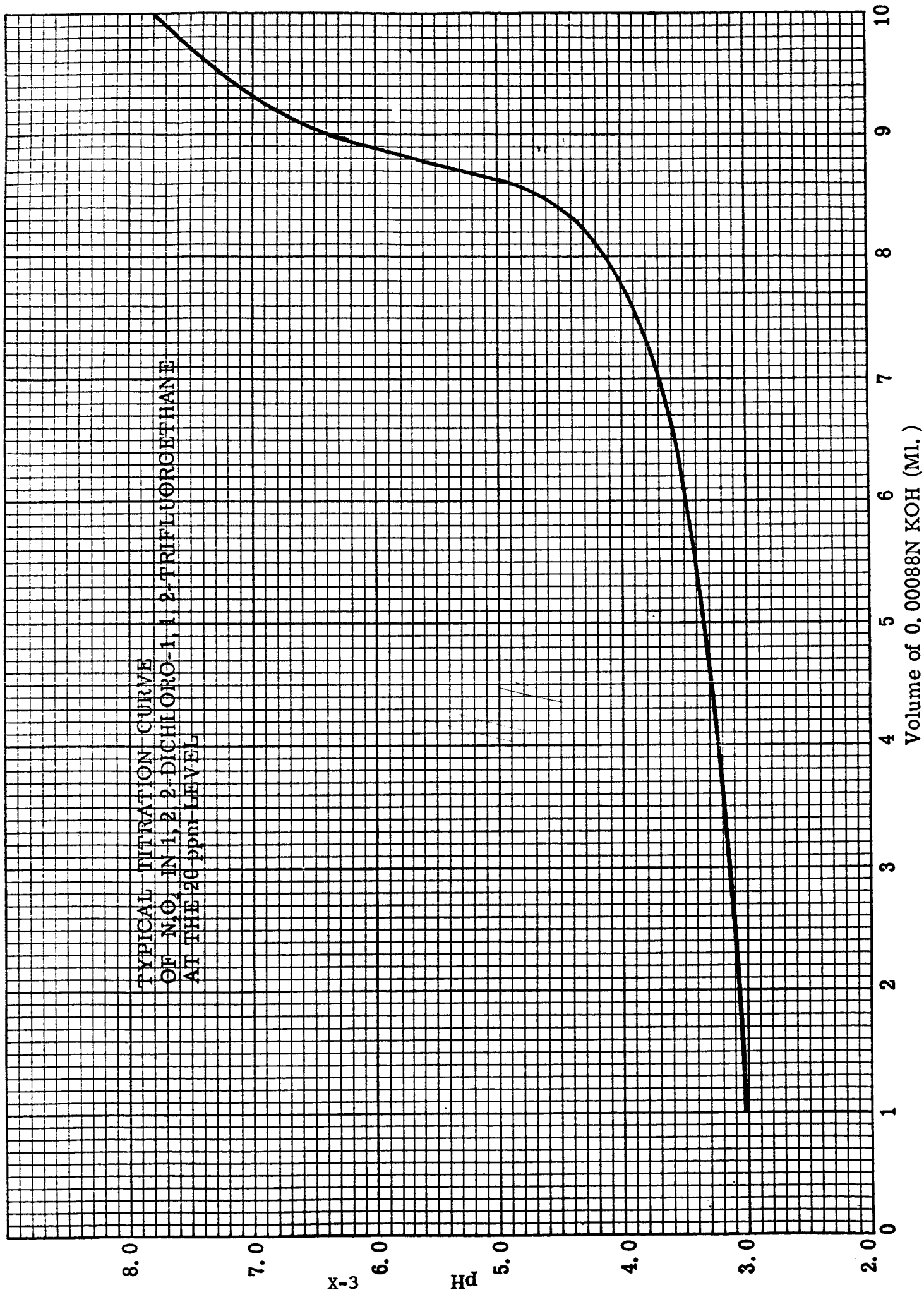
- (a) Set up the pH meter so that the solution to be titrated may be continuously monitored. Provision for continuous stirring of the sample is desirable.
- (b) Place 10 ml of ethanol in a 100 ml tall-form beaker. Add 15.0 ml of sample by pipette.
- (c) Titrate with standard alcoholic potassium hydroxide. At intervals record pH and volume of standard base. Near the end point, add the potassium hydroxide in small increments and wait for a constant reading of the pH meter.
- (d) From the plot of pH versus volume of standard potassium hydroxide, determine the volume of standard solution required for the titration and the pH at the end point. Use this indicated pH as the end point in subsequent titrations.
- (e) Titrate a blank sample consisting of 10 ml alcohol and 15 ml of organic solvent which is free of  $\text{N}_2\text{O}_4$  contamination. Correct the sample titration for this blank.

## 7. Calculation

$$\% \text{N}_2\text{O}_4 = \frac{V \times N \times 4.6}{15 \text{ ml} \times D}$$

where, V = net milliliters of standard base  
N = normality of standard base  
D = density of organic solvent in grams/ml

TYPICAL TITRATION CURVE  
OF  $N_2O_4$  IN 1,2,2-DICHLORO-1,1,2-TRIFLUOROETHANE  
AT THE 20 ppm LEVEL



## 8. Notes

- (a) Since the  $N_2O_4$  may react with the solvent, samples should be titrated immediately upon receipt.
- (b) Gas space in the sample bottle should be held to a minimum to reduce loss of  $N_2O_4$  to the vapor phase.

## C. Determination of 1,1-Dimethylhydrazine in Aqueous Solution

### 1. Scope

This method is suitable for the determination of 20 ppm or more 1,1-dimethylhydrazine in aqueous solution.

### 2. Principle

1,1-Dimethylhydrazine is titrated as a base using a strong acid as a titrant. The end point is determined using a pH meter.

### 3. Interferences

Any acid or base will represent an interference.

### 4. Apparatus

- (a) pH meter.
- (b) Magnetic stirrer and stirring bars.

### 5. Reagents

Hydrochloric acid, standard 0.1 N, 0.01 N, 0.001 N, and 0.0005 N solutions. Dilute 8.5 ml of concentrated hydrochloric acid to one liter with distilled water. Standardize against primary standard sodium carbonate. Prepare the 0.01 N, 0.001 N, and 0.0005 N solutions by diluting the 0.1 N solution with carbonate-free distilled water.

### 6. Procedure

Pipet into a beaker a volume of sample such that it contains a minimum of about 500 micrograms of 1,1-dimethylhydrazine. Place a stirring bar in the beaker and set beaker on a magnetic stirrer. Immerse electrodes in the solution and record initial pH. Add small measured portions of the appropriate standard hydrochloric acid and record pH and volume of titrant after each addition. Plot the titration curve to locate the end point and calculate ppm 1,1-dimethylhydrazine.

### 7. Calculation

$$\frac{\text{ml titrant} \times \text{normality titrant} \times 60,000}{\text{ml sample} \times \text{density sample}} = \text{ppm 1,1-dimethylhydrazine}$$

D. Determination of 1,1-Dimethylhydrazine in Nonaqueous Media

1. Scope

This method is suitable for the determination of 20 ppm or more of 1,1-dimethylhydrazine in nonaqueous media.

2. Principle

1,1-Dimethylhydrazine is titrated in nonaqueous solution by perchloric acid. The end point is determined by plotting the apparent pH as a function of volume of standard perchloric acid added.

3. Interferences

Any acid or base will represent an interference.

4. Apparatus

(a) pH meter.

(b) Magnetic stirrer and stirring bars.

5. Reagents

(a) Standard perchloric acid in ethanol, 0.1 N, 0.01 N, 0.001 N, and 0.0005 N solutions. Dilute 17.1 ml of 60% perchloric acid to one liter with 2B ethanol. Standardize against primary standard grade trishydroxymethylaminomethane using the pH meter to locate the end point. This primary standard is available from Fisher Scientific Company, Fair Lawn, New Jersey. Prepare 0.01 N, 0.001 N and 0.0005 N perchloric acid by diluting the 0.1 N solution with 2B ethanol which has been titrated to its end point with perchloric acid in ethanol.

(b) Anhydrous 2B ethanol.

6. Procedure

Pipet into a beaker a volume of sample such that it contains a minimum of about 400 micrograms of 1,1-dimethylhydrazine. Add at least an equal volume of 2B ethanol for the lower concentrations and enough to make a total volume of about 50 ml for the higher concentrations. Place a stirring bar in the beaker and set beaker on a magnetic stirrer with the pH meter electrodes immersed in the solution. Record the initial apparent pH. Add small measured portions of the appropriate standard perchloric acid and record apparent pH and volume of titrant after each addition. Plot the titration curve and determine ml of titrant at the equivalence point. Calculate ppm 1,1 dimethylhydrazine.

7. Calculation

$$\frac{\text{ml titrant} \times \text{normality titrant} \times 60,000}{\text{ml sample} \times \text{density sample}} = \text{ppm 1,1-dimethylhydrazine}$$

## XI. TECHNOLOGY SURVEY

### A. Introduction

This is a summary of a literature search for the specific technology directly related to the decontamination or the removal of trace amounts of the propellant, nitrogen tetroxide, and Aerozine-50 from propulsion systems.

The topics covered were: propellants, nitrogen tetroxide, hydrazine, and unsymmetrical dimethyl hydrazine. The subtopics were: analytical procedures, decontamination methods, hazards and toxicity, hydrazine reactions, hydrazine and related compounds' use and preparation, propellant systems storage and design, N<sub>2</sub>O<sub>4</sub> physical properties and reactions, and propellant compatibility.

The abstracting journals searched were: Chemical Abstracts (1955-65), Governmentwide Index, Technical Abstracts Bulletin (1961-65), Applied Science and Technology Index, Engineering Index, International Aerospace Abstracts, Scientific and Technical Aerospace Reports, Business Periodical Index, and Dow's Central Research Index.

The literature search, made under directions of Dr. Levis Hatch, Professor at the University of Texas, is included as an addendum to this technology survey.

### B. Decontamination Methods

The strategic missile race demands a propulsion system having instant readiness. These missiles use storable liquid propellants. The oxidizers are N<sub>2</sub>O<sub>4</sub> and white or red fuming nitric acid. The fuels are hydrazine, unsymmetrical dimethyl hydrazine (UDMH), monomethyl hydrazine (MMH), and Aerozine-50. The missiles of today are large and complex in comparison with those of earlier times. They are regularly test-fired, disassembled, inspected, and put back in standby condition. A part of this program is the decontamination of the propulsion system prior to disassembly. This requires more than passing care because the fuel and the oxidant components are highly toxic and corrosive. Both penetrate into the pores of the elastomers and the plastic materials in the propulsion system and are difficult to remove. The oxidizers form explosive mixtures with a number of solvents not normally thought of as explosive, and the fuels form explosive mixtures with air and with other oxidizing materials. Reactions between the two components and the cleansing compounds, including water, have produced undesirable solids within the systems at times. In order to maintain reliability of operation, cleanliness requirements have become more and more stringent as the complexity and size of the rockets have increased. (11) A discussion of some of the cleaning methods attempted and in use today follows.

#### 1. Decontamination by Heated GN<sub>2</sub> Purge

N<sub>2</sub>O<sub>4</sub> Removal: Of the various storable propellants, N<sub>2</sub>O<sub>4</sub> is most effectively removed by this method. However, as the N<sub>2</sub>O<sub>4</sub> is volatilized, the slight amount of water present as

in impurity in the  $N_2O_4$  lags behind and concentrates. Enough moisture can remain to form a 70% nitric acid azeotrope. This highly corrosive liquid accumulates in small crevices and cannot be removed in a reasonable time period.

A-50 Removal: Because of the higher boiling points and greater moisture content of the various fuels and blends, decontamination of the fuel system is not feasible by heated  $GN_2$  purge. (11)

## 2. Vacuum Drying

The first objection is that few systems can tolerate a vacuum. Furthermore,  $N_2O_4$  and A-50 have relatively high freezing temperatures:  $12^\circ$  and  $18^\circ$  F, respectively. Application of a vacuum causes freezing. If precautions are taken in application of vacuum to prevent freezing, moisture present as an impurity remains to form corrosive acidic or basic concentrates.

## 3. Steam Cleaning

This method has been tried in a number of instances. Although it offered several advantages, it was not considered to be wholly successful. Advantages are: a heating source to volatilize the contaminants, a purge gas to sweep the same out of the system, and a flowing liquid film flush. Disadvantages are: the formation of corrosive acidic and basic products not removable at low pressure steam temperature, and the detrimental effect of temperature in the range  $212^\circ$  to  $250^\circ$  F on nonmetallic parts.

## 4. Volatile Neutralization

Decontamination by use of volatile materials such as  $NH_3$  and  $CO_2$  were considered. However, the neutralization products are solids. In general, it was concluded that the interior of the propellant systems is no place to allow a chemical reaction producing solids to occur.

## 5. Serial Dilution

This method is a sequential filling and draining with the same water. It was found to be adequate for removing propellants to levels that are safe for experienced personnel to perform disassembly out of doors but was considered unsafe for indoor disassembly.

## 6. Use of Neutralizing Solutions

This decontamination procedure was studied by investigators at Aerojet-General Corporation for cleaning of Titan II engines. A neutralization concentrate was prepared for the oxidant and the fuel. The oxidant flushing concentrate included triethanolamine as the neutralizer, a freezing point depressant, deionized water, a wetting agent, and an antifoam agent. The fuel cleaning concentrate used as a similar formulation, but hydroxyacetic acid was substituted for triethanolamine. Also, a corrosion inhibitor



was added. The concentrates were diluted with ten parts of water and flushed through the respective systems, followed by water. The systems were dried with anhydrous methanol followed by hot  $\text{GN}_2$ . (11)

#### 7. Tri-Flush Method

This is a slight modification of the procedure discussed above except that a methylene chloride was added to the procedure.

The tri-flush method was an improvement over previously used procedures but had disadvantages as follows:

- a. Multi-flush procedure required storage and handling of large quantities of the several flushing fluids.
- b. Time-consuming.
- c. Drying was not complete.
- d. Residual antifoaming agent polymerized with solvent materials to form particulate solids.
- e. Significant corrosion was apparent. (24)

#### 8. Single-Flush Method

A new approach to decontamination was made by investigators at McDonnell Aircraft Corporation for the Gemini program which uses  $\text{N}_2\text{O}_4$  and monomethyl hydrazine as propellants. It was proposed to use a volatile solvent in single-stage flushing of both sides of the propulsion system. Freon<sup>®</sup> MF was chosen as the flushing fluid for the following reasons:

- a. It is compatible with both components.
- b. Freon<sup>®</sup> MF has low viscosity and good penetration power.
- c. The solvent adds no water to the system and is easily dried. (24)

Present decontamination of the Apollo service module uses a modification of the above system. Freon<sup>®</sup> 11 was not found to be sufficiently miscible with Aerozine-50, nor was it compatible with the materials of construction used in the fuel system. Methanol was adopted as the single flush fluid for the Aerozine system, and Freon<sup>®</sup> MF was retained for the  $\text{N}_2\text{O}_4$  system. (5)

#### 9. Other Methods

Other methods were tried, many of which are not published. An unexpected development was the discovery that trichloroethylene could form an explosive mixture with  $\text{N}_2\text{O}_4$ . Such a mixture was accidentally detonated and produced a violent explosion at Rocketdyne in 1963. (23) This explosion plus dissatisfaction with

the cleansing procedures in general, has led to renewed effort in the search for a truly satisfactory cleaning procedure.

### C. Propellant-Solvent Compatibility

In November 1963, a violent explosion resulting in the loss of two lives occurred at the Rocketdyne Company during the decontamination of an  $N_2O_4$  propellant system. It is believed that an inadvertent mixing of a trace of Aerozine-50 with  $N_2O_4$  loaded trichloroethylene detonated the solvent-oxidizer mixture.<sup>(4)</sup> Following this event, interest in compatibility testing increased. The procedure most widely followed made use of standard blasting caps in trials to determine whether a given solvent mixed in various proportions with  $N_2O_4$  would detonate. It was found that maximum sensitivity, or the tendency to explode, was obtained by placing the cap below the liquid level of a 50-50 mixture of the solvent being tested with liquid  $N_2O_4$ . A number of solvents not previously thought to be detonatable were found to be unsafe in mixtures with  $N_2O_4$ .<sup>(4,41,16)</sup> The presence of hydrogen in a solvent reduces its stability in contact with  $N_2O_4$ ; chloroform ( $CHCl_3$ ) is on the borderline but is not incompatible with  $N_2O_4$ .<sup>(16)</sup> Completely halogenated compounds such as Freon<sup>R</sup> TF (Freon<sup>R</sup> 113) and Freon<sup>B</sup> MF (Freon<sup>R</sup> 11) and carbon tetrachloride were found to be safe.<sup>(16)</sup>

### D. Properties and Reactions of the Propellants

#### 1. Aerozine-50

##### a. Properties and Reactions

Aerozine-50 is a 50/50 mixture of unsymmetrical dimethyl hydrazine (UDMH) and hydrazine ( $N_2H_4$ ). This blend is a clear, colorless, hygroscopic liquid with a characteristic fishy ammoniacal odor. The components of the mixture are miscible in all proportions. On combination, there is an immediate tendency for each to desolve in the other. But layering of the mixture can occur, with UDMH above the  $N_2H_4$ , because of the significant difference in density.<sup>(1)</sup> When first introducing UDMH and  $N_2H_4$  in a vessel or upon rapid chilling, the mixture will separate, forming an interface. Many ways of mixing the components have been studied. However, once the components have been satisfactorily blended, no appreciable stratification is observed.<sup>(46)</sup>

Aerozine-50 is soluble in water, ammonia, and alcohols; it is a strong reducing agent, and is also weakly alkaline. It will react slowly with air and  $CO_2$  to form several products and salts. Rags, sawdust, and other materials with large surface areas on prolonged exposure to the vapor, may absorb enough A-50 to ignite spontaneously.